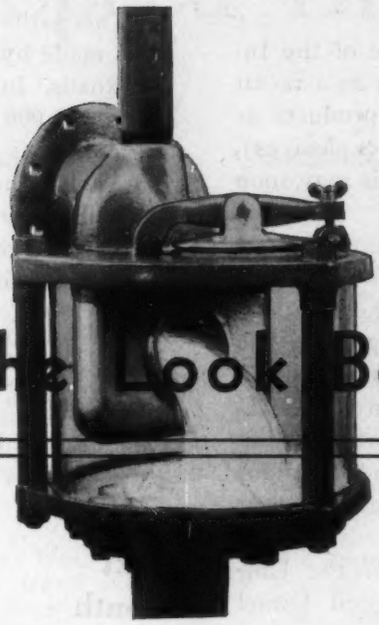
VOLUME 14, No. 6 JUNE, 1935

REFINER
AND NATURAL GASOLINE MANUFACTURER

A Gulf Publishing Company Publication



The Look Box

THE REFINER this issue enlarges its technical editorial department to much greater than usual size for the purposes of providing its readers with the complete technical and engineering program of the American Petroleum Institute's Division of Refining, Mid-Year Meeting, held at Tulsa in May. In this manner all of the important technical information brought up-to-date at the time of the meeting is presented quickly and under one cover for the convenience of those in this country unable to attend the convention, and for the many readers in foreign countries. Those who attended the meeting will find the publication of the full set of important papers of added value as a handy reference volume.

A.P.I. Refinery Technology

This program presented at the Tulsa meeting was one of the most important and valuable from an engineering and technical viewpoint, that the program committee of the division of refining has gathered together for some years. The group of papers served to bring technical data abreast of the times in several fields of endeavor. Each of the groups of papers presented at each of the three sessions at Tulsa attracted excellent attendance and spirited discussion, indicating a growing need for and a growing appreciation of technical information.

Included in the program, and reported in detail in this issue of The Refiner, were two general refining sessions and one session on progress in solvent refining. In the refining sessions such important subjects as Diesel fuels, oiliness in motor oil, and polymer gasoline from cracked gases were discussed. To reports covering progress in fundamental research on the chemical constitution of lubricating oil and the chemical constitution of the gasoline fraction of petroleum were presented. Some excellent equipment for laboratory analytical work was discussed.

In the field of solvent refining, important papers were presented at Tulsa, and are published in this issue of The Refiner, dealing with three of the solvent processes and two general papers on solvent systems and resulting products.

The authors of papers presented at this meeting have given freely of technical data secured through experience in actual functioning of processes or in actual work done and have answered many of the questions concerning progress made in technology and engineering during the past year or two; questions which have been frequently asked by many in the industry. From this viewpoint the group of papers presented in this issue are well worth studying. The Refiner takes pleasure in publishing this material this month in order that all of the technical discussions may reach its readers at an early date and in one volume.

THE American petroleum industry may soon be producing a whole new series of substances useful to man as a result of its successful separation of the naphtha fraction of petroleum, Dr. Frederick D. Rossini of the United States Bureau of Standards, told members of the American Petroleum Institute at its fifth mid-year meeting at Tulsa, Oklahoma, last month.

Wastes

Dr. Rossini, who is director of one of the Institute's research projects, states that as a result of work done on this project, such products as benzene, toluene (a constitutent of explosives), a number of xylenes and ethyl alcohols may soon be obtained from present waste.

Dr. Rossini said 35 hydrocarbons actually have been isolated and identified, six others have been detected, and the presence of 20 others is suspected. He recommended that samples of the newly-available hydrocarbons be supplied to university and other scientific research laboratories so as to permit of the accumulation of important data on their properties and behavior and to expedite the development of new economic uses for them.

Another speaker, G. C. Wilson, of the University of Wisconsin, stated that good Diesel motor fuel could be manufactured from cracked distillates, or from other residues left over from the refining of more valuable petroleum products.

Present economic advantages of Diesel operation, he said, are dependent upon a low-cost fuel, and since the refining trend is toward an increase in cracking to produce gasoline, the Diesel motor must have a fuel other than straight-run gas oil, a desirable and necessary cracking stock.

STUDY of U. S. Bureau of Census data, made by the American Petroleum Institute, has disclosed that four out of five filling stations are owned by individuals, and that more individuals are engaged in operating filling stations than in any other field of retail activity except the grocery business.

Filling Stations

The data covers 155,734 individual owners of filling stations, not including owners of some 130,000 other sales outlets, such as garages, repair shops, accessory stores, battery shops, tire shops, and motor vehicle dealers, most of which also retail petroleum products.

It is estimated that 70 percent of the filling stations do a business amounting to less than $10,000 a year. Business for the average station is slightly below $9,000 a year. One lone station is an exception. Its yearly sales exceed a million dollars.

The 170,404 filling stations in the United States provide full-time employment for 143,395 workers. In addition, individual owners often are assisted by members of their families, and by part-time workers.

Other studies of the Institute in the marketing field have revealed that the average filling station customer buys 600 gallons of gasoline yearly. This estimate recently was confirmed by surveys made by the United States Bureau of Public Roads. In the course of a year more than 15,000,000,000 gallons of gasoline flow through the country's 750,000 gasoline pumps. It is estimated that the average pump dispenses less than 60 gallons per day, a substantial reason why the gasoline buyer never waits for service at an American filling station.

"CALIFORNIA DEVELOPMENT NUMBER" is the name selected for next months' issue of THE REFINER. At this time a group of 12 articles will be presented describing various refining and natural gasoline installations in California.

Next Month

Since the early days at Kettleman Hills the problems of drilling and production of oil have received a great deal of attention. In regard to the problems of gas transportation, gas gathering, mixing and gasoline extraction but little has been published. In the July issue there will be three articles dealing with the gas problems in that great field. These articles are as follows, "Handling Gas at Kettleman Hills," "Design and Operation of Kettleman Hills Gas Mixing Station," and "Kettleman Hills Natural Gasoline Plants."

These three interesting and valuable discussions designed to incorporate all of the problems and practices in gas handling and gasoline extraction prevailing at this time, were prepared for exclusive presentation in THE REFINER by John C. Albright, through the cooperation of executives and engineers with Kettleman Hills North Dome Association.

Included in the July issue is a complete list of California refineries and refining companies, giving personnel and type of processing facilities in use. In addition there will be articles describing a large West Coast solvent refining installation, two articles dealing with stabilizing systems, one on continuous treating and one on combatting corrosion.

The important series of articles on Inspection of Oil Refinery Equipment, by F. L. Newcomb, will be resumed. Part four of this series deals with records and forms required for proper functioning of the inspection department.

(*Continued on page* 39a)

Fuel Specifications for High-Speed Diesel Engines

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THE development of the high-speed Diesel engine depends as much upon proper fuel specifications as upon engine design. Therefore, refiners and engine builders will find it advantageous to cooperate in solving fuel problems.

The various items included in specifications are discussed briefly. The importance of ignition quality and its effect on engine operation are emphasized. Units of its measurement are defined.

Typical specifications, as used by various engine builders, refiners, and operators have been grouped in tabular form to show the spread in present limitations. Some of the classifications proposed by the American Society for Testing Materials have been included in the table for comparison. These may well be used as a basis for working out more uniform specifications.

The low cost of fuel oil is due to its position as a by-product of refineries, so that the same emphasis cannot economically be placed upon its refinement as in the case of motor gasoline. However, the proper selection of the fuel from pertinent specifications will enable an engine user to obtain good operation at a minimum fuel cost.

This paper was presented at the Fifth Mid-Year Meeting, American Petroleum Institute, Tulsa, May 15, 1935.

THE necessity for cooperation between refiner and engine builder in the matter of Diesel fuel is so obvious that there is little need for supporting arguments. As an example of what can be accomplished, consider the phenomenal development of the gasoline engine in recent years. Much of this advance has been due to parallel developments in both engine design and fuel characteristics. There is just as large an opportunity ahead for advancement in improving Diesel engine operation. In the case of the Diesel as compared to that of the gasoline engine, the problem is even more pressing; and it is also more difficult, because the present trend is in the opposite direction, to the economic trend of refinery practice. It is generally understood that there will be an increase in the amount of cracking of petroleum products to produce gasoline. If the high speed Diesel engine is to continue to enjoy its present economic advantage in the matter of low priced fuel, it must not compete in the market for the straight-run gas oil, which is a desirable and necessary cracking stock.

The old idea that a Diesel engine should burn anything has been made completely obsolete by its entrance into the higher speed fields. In fact, the idea had an evil influence from its conception. It only encouraged the operator towards carelessness with regard to both fuel selection and the matter of avoiding contamination. In each case where someone has operated a Diesel engine on some freak fuel, he has neglected to state how long the engine would operate on such a fuel.

ENGINE DESIGN CAN BE, AND IS BEING, MODIFIED

Much can be done in the matter of changing both fuel and engines better to adapt them to each other. Compression ratios can be modified within a limited range. Increasing the compression ratio will help solve fuel-ignition problems, but usually increases the maintenance problems. The engine designer can make changes which affect the temperature of some particular part or parts of the combustion chamber. Pump design, manner of fuel injection, and control of air and gas movement during combustion, as well as control of combustion itself, offer opportunities of solving problems that might otherwise require the use of more costly fuel for satisfactory operation. Air and gas movement during combustion in solid injection engines is being controlled at the present time by four general types of combustion chambers: viz., the open head, the pre-combustion chamber, the divided chamber, and the air cell arrangement.

PRESENT DIESEL-FUEL SPECIFICATIONS

In order to determine the limits of present Diesel fuel specifications, a tabulation of limits has been set up from a study of available specifications. Table 1 shows how the limits of actual specifications compare with the classification offered by Committee D-2 of the American Society for Testing Materials (A.S.T.M.). These data do not represent a complete survey by any means, but they do show a rather wide spread in values as stated by different companies. The A.S.T.M. offers data for two more classes of Diesel fuel oil, but they have not been included in this table. It is obvious that greater uniformity in specifications would simplify matters, and the A.S.T.M. proposal is a step in the right direction.

PROPERTIES OF DIESEL FUELS

Committees that have studied the Diesel fuel situation seem to be agreed that viscosity and ignition

TABLE 1
Typical Diesel Fuel Specifications—1935

	Speeds Over 1,000 R. P. M.		Speeds Under 1,000 R. P. M.					
	ASTM 1-D	Manufacturers, 12 Companies	ASTM 3-D, Over 360 R. P. M.	Manufacturers, 5 Companies	Refiners, 5 Reporting	Railroads, 5 Reporting	Navy	ASTM 4-D, Speeds Not Over 400 R. P. M.
Gravity, deg. API	.....	24–36	.....	30–70	28–36	28	.....	.....
Viscosity, Saybolt Universal, at 100° F., sec. (minimum)	32–50	30–100	32–70	35–150	40–60	35–70	.....	500 maximum
Pour point, °F. (maximum)	35	0–30	35	0	0–15	0–35	0	35
Carbon residue, percent (maximum)	0.2	1.0	0.5	0.5	0.05–1.25	0.5	0.5	3.0
Sulfur, percent (maximum)	.....	0.5–2.0	.....	0.3–1.5	0.63–1.50	0.5–1.0	1.0	.....
Asphaltum, percent (maximum)	.....	1.0	.....	0.3	.....	.....	0.5	.....
Bottom sediment and water, percent (maximum)	0.05	nil-1.0	0.20	Trace–1.0	0–0.5	0.1–0.3	0.05	0.6
Ash, percent (maximum)	0.01	0.02–0.05	0.02	0.05	Trace–0.05	0.05	0.01	0.04
Flash point, °F. (minimum)	115	150	150	150–190	Open cup 150–260	150	150	150
Ignition Quality:								
Cetene No. (minimum)	*50	50–60	*40	50	.....	52	.....	*30
Diesel index (minimum)	*45	37–47	*30	.....	.....	.....	.....	*20
Critical-compression ratio	*81	.....	*8.8	.....	.....	.....	.....	*9.8

ASTM fuel-oil classification, reference No. 15.
*Suggested.

characteristics are the two most important properties. The problem of ignition rating will be discussed later.

Viscosity of Diesel fuel is usually stated in Saybolt Universal seconds at 100°F., although in some cases it is also specified at a lower temperature. It is an important property because of the necessity for lubricating the fuel pump. Moreover, the rate of burning of the fuel is retarded with the increased drop size, which results from increased viscosity.

Bottom sediment and water (B. S. & W.) are usually stated in percent, and the maximum allowable stated in specifications. The limits vary from nil to one percent. This item has come to be more of a problem as manufacturers go to smaller orifices in the nozzles for the open type heads and the smaller cylinder bores of the high speed engine. Various types of filters have been only partly successful in taking out the very fine material which increases wear and partly clogs nozzles to cause poor fuel distribution.

Pour point is important if engines are to be operated outdoors in cold weather. Either the fuel must run to the pump at the atmospheric temperature or heat must be supplied to raise its temperature above the pour point. Some engine manufacturers state that the pour point must be 10 to 15 degrees below the minimum operating temperature.

It is a little difficult for one to feel that vapor lock in Diesel fuel lines will become a serious matter, although the American Committee at the World Petroleum Congress expressed the belief that it was a problem.

The maximum allowable sulfur content is commonly limited at about 1 to 1.5 percent. Within reasonable limits, the amount of sulfur that can be handled without harmful effects seems to be mostly a matter of conditions of operation. Corrosion has been reported in crankcases and in places where the moisture of the exhaust condenses. Sulfur is apt to be more of a problem for intermittent operation during cold weather conditions.

Conradson carbon tests show the residual content of the fuel when distilled or burned with insufficient air. Many engine manufacturers feel that, in the absence of a better test, it serves a useful purpose in the specifications. The only purpose of altering the test would be more nearly to simulate conditions as they occur in the actual engine. The specification undoubtedly limits the amount of heavy residue stock that may be added to the blend.

In the case of overhead distillates, the ash content is negligible. It is not specified extensively, but it might be used as a means of keeping down the proportion of residual stock in the blend. Asphaltum content and neutralization number are not used to any extent in present specifications, and are generally considered to have but little, if any, value.

Flash point is included only to limit the fire hazard during storage and handling. It is given no meaning in regard to engine performance. Gravity is expressed in units of the A.P.I. scale. When taken alone, it is not always a safe criterion. However, when considered with other properties, such as viscosity, it becomes a measure of the paraffinicity of an oil.

Boiling range or volatility of Diesel fuel appears in only a small portion of the available specifications. Four companies, out of 16 reporting, state maximum initial points from 380 to 450°F., and 90 percent points of 675 to 700°F. In place of the initial point, two companies state the 10 percent point as 460°F. Four of these same companies state end points of 696 to 750°F. There is some disagreement among authorities as regards whether or not the fuel must evaporate before it burns. However, there is agreement that a fuel's volatility taken alone does not permit one to judge its behavior during the period of ignition.

IGNITION QUALITIES

Recent combustion studies have made possible a better selection of Diesel fuel to fit engine requirements. The objection to ignition lag is that it allows the fuel entering the combustion chamber to accumulate for an instant. Then, when it starts to burn, the entire quantity in the chamber burns suddenly and causes roughness of operation. Also, a fuel of poor ignition qualities causes starting difficulties. With a better knowledge of ignition lag has come the development of a system for measuring this characteristic of the fuel. Moreover, it has been necessary to establish a unit of measurement.

Cetene number seems to be the most generally-accepted unit at the present time. Cetene is a pure chemical, and is used in the same manner as octane is used for rating gasoline—although its behavior in an engine is just opposite. Cetene number is defined as the percentage of cetene in a blend of cetene and alphamethyl-naphthalene which has the same ignition quality as the fuel under test. The tests must be

carried out in a specified engine under a definite set of engine conditions. It may be determined by bracketing the unknown between two known fuels just as for octane rating; or it may be determined from the critical compression ratio, and read from a calibration curve previously determined for the engine.

Critical compression ratio must be determined on a C. F. R. engine as modified to run as a Diesel engine. The critical compression ratio is obtained by motoring the engine at 600 r.p.m. and noting the compression ratio at which firing occurs within three seconds after the fuel has been injected.

NEW TYPE C.F.R.-DIESEL FUEL TEST ENGINE

Experiments are being made to determine whether or not better correlation of results can be obtained between different laboratories by the use of an entirely re-designed head for this engine. It uses a divided combustion chamber which permits changing the compression ratio by adjusting the position of a plug. Also, this engine may be used to rate fuels by measuring the ignition delay with a modified bouncing pin arrangement.

The relation between cetene number and critical compression ratio (C.C.R) is given in Table 2. This relation is necessarily approximate, for its actual value will differ somewhat for different engines. Cetene number seems to have an advantage in that its values are well distributed over the range of Diesel fuels. Rendel states that the general range of fuels from American crudes lies between 33 and 75 cetene numbers, while gas oils from cracked stocks vary from about 35 to 55. Foster gives:

	Cetene No.
Straight-run Mid-Continent gas oil	60
Straight-run West Texas gas oil	45-55
Mixed Mid-Continent cracked furnace oil	40-45
Liquid-phase cracked distillate bottoms	40-45
Vapor-phase cracked distillate bottoms	30 +

Diesel index number may be calculated from aniline point and A.P.I. gravity at 60°F. It is the product of the two divided by 100.

Aniline point is the lowest temperature (°F.) at which equal parts by volume of freshly distilled aniline and the test sample of oil are completely miscible. It is determined by heating such a mixture in a jacketed test tube to a clear solution and noting the temperature at which turbidity appears as the mixture is cooled.

Diesel index has the advantage of being easily determined in the field, and gives a fair approximation of the ignition rating.

Moore and Kaye have proposed using a viscosity-gravity constant as rating for ignition qualities. They have worked out an equation that involves the use of specific gravity (at 60°F.) and kinematic viscosity at 100°F. (in millistokes). The viscosity-gravity constant can be determined and converted to cetene numbers by chart, or the cetene number can be determined directly from the viscosity and gravity. This permits obtaining approximate cetene numbers without a test engine. They claim an accuracy of about plus or minus two cetene numbers for most fuels.

Heptane number: The percent of heptane blended with octane to match the unknown fuel has been proposed as a unit for rating ignition quality of Diesel fuel. Table 2 shows that heptane numbers do not cover completely the range of Diesel fuels.

TABLE 2

Approximate Conversion Chart for Diesel-Fuel Ignition Ratings

A Cetene No.	B C.C.R.	C Diesel Index	D Heptane No.	E Remarks
30	12.0	..	33	
35	11.0	11	41	Rough fuel.
40	10.0	18	56	OK in well-designed high-speed engines
45	9.1	27	85	
50	8.5	35	100	
55	8.2	42	..	Good fuel.
60	7.9	46	..	May be noisy in some engines at light loads.
65	7.7	53	..	
70	7.6	56	..	
75	7.4	59	..	

B and C—See reference 17.
D—See reference 1.
E—See reference 22.

FUEL DOPES

It is not thought that cetene rating of Diesel fuels will become anywhere near so important as octane rating now is for the gasoline engine. However, the possibility exists of using dopes to hasten ignition in

(*Continued on page 306*)

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UNIONTOWN
Fuel Data Correlation
at Various Manifold Temperatures

NEIL MacCOULL,
Chairman

GRAHAM EDGAR,
C F R Detonation Subcommittee

D. P. BARNARD,
Special Subcommittee

AT THE September 17, 1934, meeting of the Detonation Subcommittee[2] a motion was passed to "investigate the effect of correlation with the present road data, of laboratory ratings made at manifold temperatures of 200, 225, 250, 275, and 300° F." Direction of this investigation was placed in the hands of a special subcommittee consisting of Messrs. Neil MacCoull, D. P. Barnard, and Graham Edgar. Arrangements were then made for the reserve stocks of Uniontown gasoline to be shipped in one-gallon cans to one of the special subcommittee members, who coded and shipped them to the testing laboratories of the Detonation Subcommittee members. Operating instructions were mailed on October 18 and November 19, 1934, to the same laboratories, so that a uniform test procedure would be used by all. (See Appendices 1 and 2 for these instructions).

DATA

The rather voluminous data have been compiled in the attached 11 tables. Tables 1 to 5, inclusive, give the anti-knock values obtained at manifold temperatures of 200, 225, 250, 275, and 300° F., respectively, in terms of percent reference fuel C-8 in A-3. Averages are shown for each fuel by all laboratories, as well as for each laboratory on all fuels. The former were of value in establishing a statistical value for each fuel, while the latter were of value in determining the mean deviation of each laboratory from the statistical average.

These averages do not include the Standard Oil Company of California, since they gave data for only three of the five temperatures, and it was considered desirable to average the same laboratories in all cases. It is of interest to note that in submitting their data, this laboratory stated that only three temperatures had been reported, because they had found a straight line relationship between anti-knock value and manifold temperature.

FUELS

All branded commercial fuels were taken from reserve stocks of the same fuels used at Uniontown, except fuel No. 4, which was omitted because of insufficient stock. The research fuels, however, (b-1 to b-9, inclusive) were blended from reserve stocks of their components. A comparison of the anti-knock values obtained at 300° F. with those originally made for the road test correlation, indicate an almost universal depreciation; and, strangely enough, the two cracked Research Fuels showed the least change.

[2]See page 6, minutes of meeting of September 17, 1934.

THE prime object of this work was to determine if the A. S. T. M. anti-knock method would give better correlation with the Uniontown road data by operating at some manifold temperature lower than 300° F. While the average of all fuels in all Uniontown cars was only 0.36 of an octane number higher than by the A. S. T. M. method, some fuels showed deviations of 1 to 2 octane units; and it was thought that lowering the manifold temperature might bring these extreme cases into better alignment, while not lowering the average further from true correlation. It was found that while lowering the manifold temperatures raised the values for some fuels about twice as much as others, the anti-knock values of those fuels showing the poorest correlation by the A. S. T. M. method were, in general, changed but little more than the fuels showing good correlation.

The mean anti-knock value[1] of all fuels tested was found to rise 2.0 octane numbers for each 100° F. drop in manifold temperature. Thus, average correlation with the Uniontown values would result at a manifold temperature of about 280° F.; while at 260° F. the average deviation would equal that found for 300° F., but would be of opposite sign. In other words, while the C. F. R. Committee, in general, felt that the agreement with the A. S. T. M. method was satisfactory, any manifold temperature from 260 to 300° F. would have given an agreement as good or better.

This applies only to the average values of all fuels. An interesting feature developed was that segregation of the fuels into two groups, consisting of the Branded Commercial gasolines and the Research Fuels, revealed widely different results, in spite of the fact that both groups were of essentially similar composition. Average correlation with the Uniontown Hill data for the latter group would have resulted at a manifold temperature of only 237° F., but the former group would have required 340° F., a difference of 103° F.

A secondary object of this investigation was to determine if in rating these Uniontown gasolines the deviations between different laboratories were influenced by the manifold temperature. It was found that the mean deviation was reduced as the temperature was reduced.

This report was presented at the Mid-Year Meeting, American Petroleum Institute, May 15, 16, 1935, at Tulsa.

[1]In terms of the standard reference fuels.

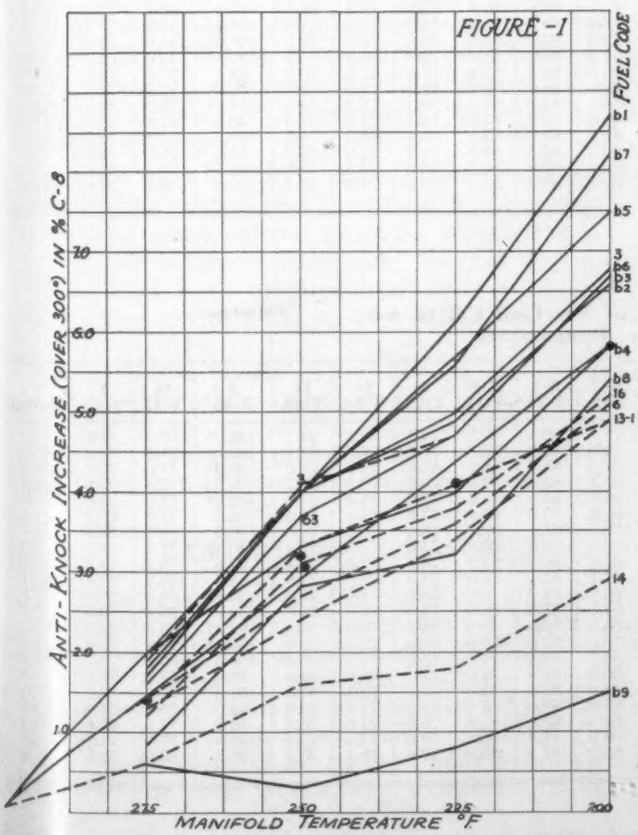
Uniontown Code Number	A.S.T.M. Rating (300°F.) Percent C-8 in A-3		
	Avg. Original A & B Series	New or T-Series	Difference
1	72.0	69.4	—2.6
3	98.0	95.9	—2.1
6	76.0	73.3	—2.7
13	73.5	70.2	—3.3
14	22.5	20.9	—1.6
16	78.0	74.2	—3.8
b-1	80.0	80.4	+0.4
b-2	65.0	64.6	—0.4
b-3	65.0	64.5	—0.5
b-4	60.0	57.8	—2.2
b-5	79.0	77.3	—1.7
b-6	75.0	71.7	—3.3
b-7	90.0	88.2	—1.8
b-8	71.0	70.2	—0.8
b-9	84.0	82.3	—1.7
Average.....	72.6	70.7	—1.9

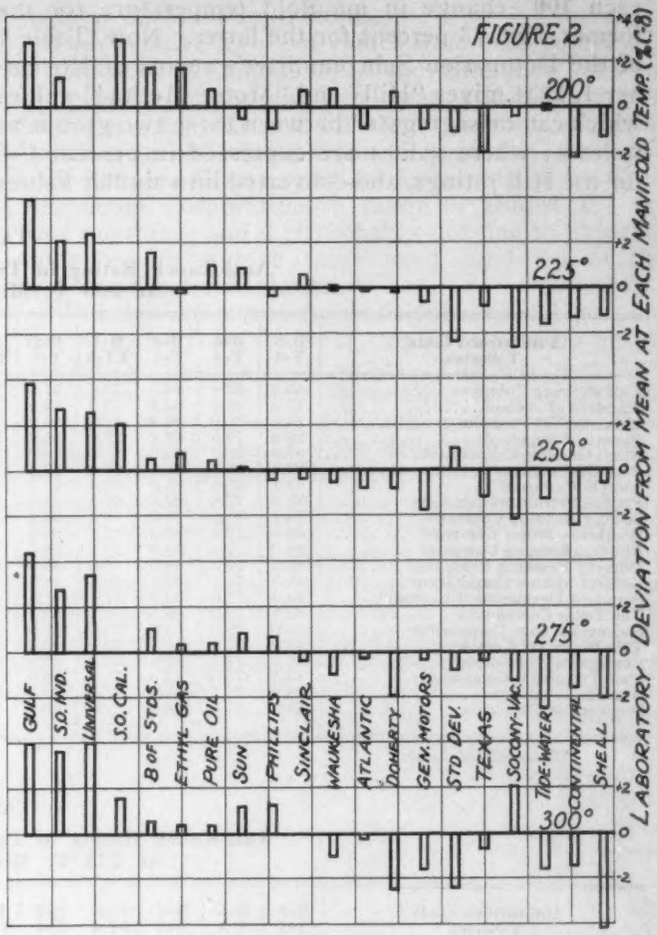
This change in anti-knock values makes it somewhat difficult to make a correlation with the road data; but the liberty has been taken of assuming that the anti-knock rise, due to lowering the manifold temperature, is about the same for the samples when tested this last time as when tested previously. For this reason, Figure 1 has been prepared, showing the rise of anti-knock value for each fuel at non-standard manifold temperatures. A heavy straight line has been drawn through the circles which represent the average values at each temperature. While two of the circles do not fall on this line, they are only 0.3 percent C-8 off, or about 0.1 of an octane unit, which may be considered within the limits of error.

Figure 1 is of particular interest for the following reasons: viz.,

1. It appears that a straight line relation exists between manifold temperature and anti-knock values.

2. Fuel b-1 is only slightly more sensitive to temperature than the next two most sensitive fuels, and is not radically different in this respect from most of the group. This is contrary to what might be expected from a consideration of the differences between the Research Method and the Motor Method for these fuels, the difference being almost twice as great for fuel b-1 as the next most sensitive fuel.





3. Even fuels such as b-9, the California Straight Run, and No. 14, which is assumed to be a straight run product, show a rise in anti-knock value with decreasing manifold temperature.

4. The benzol blend, b-8, is not particularly sensitive to temperature, being less sensitive than the average.

5. The branded fuels, indicated by dotted lines are, in general, less sensitive than the research fuels, which are indicated by the solid lines. Thus, the research fuels might be expected to be more difficult to correlate, and to require a higher jacket temperature for this purpose, because the branded group are more similar to straight run fuels which are relatively immune to temperature.

6. Average correlation with the Uniontown Hill ratings would result from use of a manifold temperature of 280° F. (since the average of all ratings obtained on the road was 0.36 of an octane number, or 1.05 percent C-8 higher than the average of all fuels by the A. S. T. M. method); and lowering the temperature an equal amount again (to 260° F.) would result in the same average deviation between the two methods, but of opposite sign.

It is interesting at this point to segregate the research fuels from the branded fuels, for, as shown in 5 above, the former group was more sensitive than the latter, the sensitivity being 6.3 percent C-8 for

each 100° change in manifold temperature for the former, and 4.3 percent for the latter. Now, Table 7 of the Detonation Subcommittee's report of November 1, 1934, gives "Hill" and "Motor Method" values which can be segregated between these two groups as follows; where values are expressed in percent C-8 for the Hill ratings, and converted into similar values from the A. S. T. M. octane numbers by the calibration curve II (e)—1 of the Data Book:

	Research Group	Branded Group
Hill Rating	78.0% C-8	64.5% C-8
A. S. T. M. Rating	74.5%	66.6%
Difference	+3.5%	—2.1%

From these data, and by making use of the sensi-

TABLE 1

Anti-Knock Rating in Terms of Per Cent C-8 in A-3 At 200° F. Mixture Temperature

Uniontown Code / T-Series	B-5 T-3	B-6 T-4	B-4 T-5	B-3 TT-6	B-7 T-7	B-8 TT-8	B-2 T-9	B-1 T-10	B-9 T-11	6 T-12	13 T-13	14 T-15	3 T-16	16 T-17	1 T-18	Average
Gulf Refining Company	88.5	80.8	64.3	74.4	97.9	78.1	75.6	91.7	89.8	78.8	77.5	24.5	106.0*	81.9	77.5	79.2
Standard of Indiana	87.8	80.7	64.5	73.0	99.0	71.2	71.3	91.5	85.5	79.2	77.0	22.0	104.0*	81.7	77.5	77.8
Universal Oil Products	84.0	80.0	64.0	71.0	96.0	73.0	77.0	87.0	85.0	78.0	73.0	23.0	106.0*	78.0	73.0	76.5
Bureau of Standards	86.4	79.9	66.4	72.8	95.2	82.6	71.8	89.1	87.3	79.6	76.8	25.5	104.0*	79.9	75.5	78.2
Ethyl Gasoline Corporation	87.0	80.0	65.0	73.0	98.0	78.0	73.0	92.0	82.0	80.0	78.0	23.0	104.0*	82.0	77.0	78.2
Pure Oil Company	84.5	78.6	65.8	67.5	97.5	79.0	70.5	87.0	86.0	81.2	77.0	24.0	106.8*	80.6	70.6	77.2
Sun Oil Company	84.4	80.0	63.0	70.5	97.1	75.2	70.0	86.9	83.8	78.5	76.1	23.5	101.0*	79.2	70.0	76.0
Phillips Petroleum Company	83.3	77.8	62.8	69.5	93.5	73.0	70.0	85.8	84.3	77.8	76.3	22.5	99.5	80.5	76.8	75.5
Sinclair Refining Company	84.2	81.5	67.0	70.8	95.5	74.0	72.4	90.3	83.9	78.5	75.2	28.5	100.0	82.0	74.5	77.2
Waukesha Motor Company	85.6	77.6	65.0	72.4	95.6	76.4	71.9	94.0	84.0	78.0	75.1	21.4	107.0*	79.4	76.6	77.3
Atlantic Refining Company	84.0	77.0	63.0	70.0	99.0	73.0	71.0	88.0	83.0	79.0	74.0	20.0	100.5*	81.0	70.0	75.5
Doherty Research Company	85.5	79.0	64.0	73.0	99.0	81.0	70.5	93.0	82.5	77.0	74.0	25.0	103.0*	77.0	73.0	77.1
General Motors Corporation	81.8	74.6	61.8	70.2	94.7	76.8	70.3	85.6	84.1	78.5	75.8	25.7	100.0	76.6	77.7	75.6
Standard Development Company	84.0	78.0	62.0	71.0	97.0	77.0	70.0	88.0	82.0	79.0	75.0	22.0	105.0*	80.0	70.0	76.0
The Texas Company	82.0	76.3	59.5	69.3	93.7	74.5	69.0	87.0	82.0	75.5	73.0	22.7	104.0*	75.8	74.5	74.6
Socony-Vacuum Corporation	85.0	78.0	64.0	72.0	97.0	75.0	71.0	90.0	81.0	78.0	71.0	25.0	100.5*	79.0	75.0	76.1
Tide Water Oil Company	87.0	77.5	62.5	73.0	95.5	73.5	71.0	90.5	83.5	79.0	74.5	24.5	100.0	79.0	76.0	76.5
Continental Oil Company	82.0	77.5	62.0	68.0	93.5	71.0	68.0	87.0	81.0	78.0	74.0	22.0	100.0	77.5	74.0	74.4
Shell Petroleum Company	84.5	77.0	63.0	71.5	96.0	74.0	68.0	87.5	81.5	76.0	73.0	28.0	100.5*	76.5	71.5	75.2
Average	84.8	78.5	63.6	71.2	96.4	75.6	71.2	89.1	83.8	78.4	75.1	23.8	102.8*	79.4	74.3	76.5
Standard of California	88.5	81.8	68.0	78.0	96.6	78.2	77.2	95.0	85.2	80.9	77.6	23.3	100.0	82.6	77.4	79.4

*Extrapolated value.

TABLE 2

Anti-Knock Rating in Terms of Per Cent C-8 in A-3 At 225° F. Mixture Temperature

Uniontown Code / T-Series	B-5 T-3	B-6 T-4	B-4 T-5	B-3 TT-6	B-7 T-7	B-8 TT-8	B-2 T-9	B-1 T-10	B-9 T-11	6 T-12	13 T-13	14 T-15	3 T-16	16 T-17	1 T-18	Average
Gulf Refining Company	88.5	80.8	64.2	73.8	97.8	77.5	73.2	90.6	89.2	78.2	77.5	24.1	107.0*	81.5	76.3	78.7
Standard of Indiana	86.2	79.7	63.2	71.5	97.5	71.2	71.0	90.7	85.0	78.6	76.0	21.5	102.5*	81.4	77.1	76.9
Universal Oil Products	86.0	80.0	61.0	70.0	98.0	72.0	75.0	87.0	85.0	79.0	73.0	22.0	105.0*	77.0	74.0	76.2
Bureau of Standards	83.1	77.6	64.3	71.9	93.4	79.7	69.4	86.3	84.0	78.1	75.2	24.2	101.2*	79.1	77.0	76.3
Ethyl Gasoline Corporation	82.0	76.0	62.0	68.0	96.0	72.0	69.0	85.0	81.0	77.0	77.0	21.0	102.5*	77.0	73.0	74.6
Pure Oil Company	83.5	77.5	63.9	66.8	96.8	77.4	69.1	85.6	85.0	79.1	75.7	23.0	105.0*	79.0	70.0	75.8
Sun Oil Company	82.2	80.0	64.1	70.5	96.5	74.3	70.5	86.5	83.7	77.8	76.0	22.5	101.0*	80.0	70.5	75.7
Phillips Petroleum Company	82.0	76.5	61.5	68.5	92.5	71.5	69.0	84.5	84.5	77.0	74.5	22.5	99.5	79.0	74.5	74.5
Sinclair Refining Company	83.2	80.0	65.5	67.2	94.5	73.0	70.4	86.8	82.7	77.7	43.5	25.5	99.5	80.0	71.0	75.4
Waukesha Motor Company	82.9	74.7	62.0	70.5	94.0	73.0	70.0	89.0	83.4	75.0	74.0	21.2	100.0	78.5	74.3	74.8
Atlantic Refining Company	84.0	76.0	63.0	70.0	96.0	73.0	70.0	85.0	83.0	76.0	74.0	20.0	100.5*	80.0	70.0	74.7
Doherty Research Company	82.5	77.0	61.5	69.5	89.0	77.0	69.0	91.0	81.0	75.0	74.0	24.5	102.5*	75.0	71.0	74.6
General Motors Corporation	80.7	74.9	59.6	68.7	91.7	73.3	68.3	86.5	83.6	77.6	74.4	23.3	98.4	77.0	74.0	74.2
Standard Oil Development	82.0	75.0	57.0	69.0	90.0	69.0	70.0	85.0	79.0	75.0	72.0	18.0	97.0	77.0	71.0	72.4
The Texas Company	81.2	75.5	59.5	68.8	92.5	75.0	69.0	85.2	81.0	76.3	72.4	23.0	101.0*	75.3	74.4	74.0
Socony-Vacuum Corporation	81.0	74 0	61.0	64.0	90.0	70.0	66.0	83.0	81.0	75.0	72.0	23.0	96.0	77.0	70.0	72.2
Tide Water Oil Company	82.0	71.5	59.5	68.5	90.5	71.0	67.0	83.0	83.0	74.5	74.5	24.5	100.0	74.5	73.5	73.2
Continental Oil Company	82.0	76.0	60.0	67.0	93.0	71.0	68.0	85.5	82.0	77.5	74.0	22.0	96.0	76.0	73.0	73.5
Shell Petroleum Company	81.0	74.5	61.5	70.5	91.0	74.0	67.0	87.0	82.0	76.0	72.5	26.0	96.5	76.5	68.0	73.6
Average	83.0	76.7	61.8	69.2	93.8	73.4	69.5	86.5	83.1	76.9	74.3	22.7	100.6	78.0	72.8	74.8

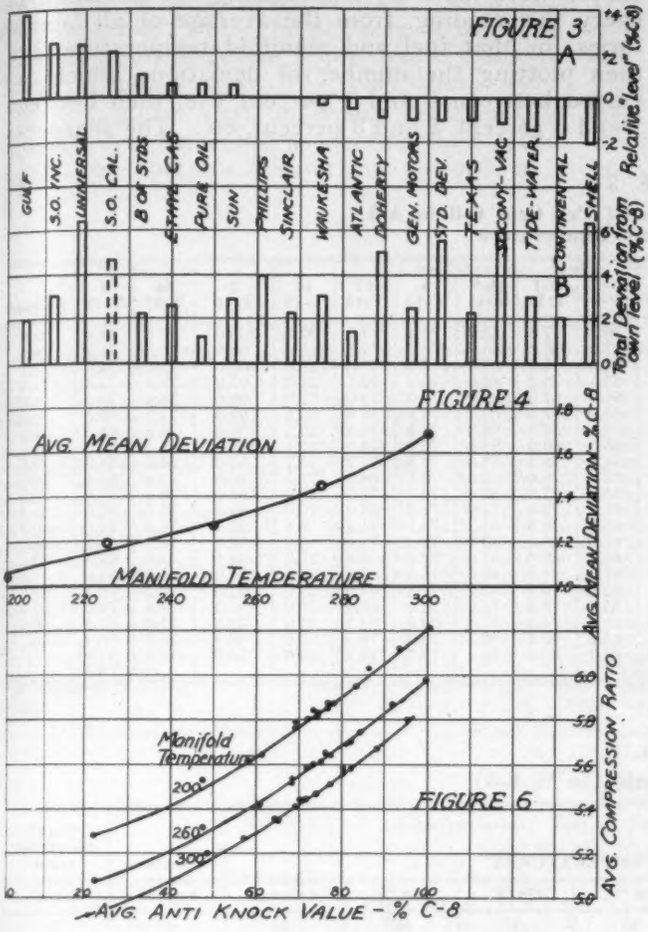
*Extrapolated values.

TABLE 3

Anti-Knock Rating in Terms of Per Cent C-8 in A-3 At 250° F. Mixture Temperature

Uniontown Code / T-Series	B-5 T-3	B-6 T-4	B-4 T-5	B-3 TT-6	B-7 T-7	B-8 TT-8	B-2 T-9	B-1 T-10	B-9 T-11	6 T-12	13 T-13	14 T-15	3 T-16	16 T-17	1 T-18	Average
Gulf Refining Company	86.4	79.9	64.3	71.8	96.3	76.9	71.3	90.4	87.7	78.1	76.5	24.1	106.0*	80.5	75.8	77.7
Standard of Indiana	85.3	79.0	63.7	70.8	96.7	72.3	70.6	89.0	86.0	78.5	76.5	21.7	100.2*	81.5	77.3	76.6
Universal Oil Products	82.0	80.0	64.0	70.0	96.0	72.0	77.0	86.0	85.0	81.0	74.0	22.0	108.0*	77.0	73.0	76.5
Bureau of Standards	80.5	76.4	61.5	70.2	91.7	77.8	67.5	83.8	81.9	76.5	73.6	22.3	99.5	77.6	75.6	74.4
Ethyl Gasoline Corporation	82.0	78.0	63.0	68.0	95.0	72.0	69.0	85.0	82.0	77.0	75.0	21.0	102.5*	77.0	73.0	74.6
Pure Oil Company	82.0	76.4	62.2	65.6	94.6	76.2	68.0	83.0	83.8	77.2	74.1	22.2	103.0	77.5	68.8	74.3
Sun Oil Company	82.2	76.5	61.6	70.0	93.6	72.8	70.0	83.8	82.0	76.5	73.6	20.0	100.0	78.2	69.0	74.0
Phillips Petroleum Company	80.0	75.3	61.5	67.6	90.3	72.3	68.0	83.0	83.8	75.8	73.3	22.8	97.5	77.5	74.5	73.5
Sinclair Refining Company	81.2	77.5	61.8	65.8	92.2	72.4	67.8	86.3	82.5	75.0	72.5	25.4	97.0	76.2	71.0	73.6
Waukesha Motor Company	80.8	73.8	60.0	68.3	92.8	70.9	68.4	85.8	83.6	74.4	71.9	21.8	98.5	78.2	72.5	73.4
Atlantic Refining Company	80.0	74.0	63.0	70.0	91.0	73.0	69.0	81.0	82.0	75.0	73.0	20.0	100.5*	77.0	68.0	73.1
Doherty Research Company	80.5	73.5	59.0	67.0	92.5	75.5	67.5	85.0	81.0	74.5	73.0	24.5	100.0	75.0	70.0	73.2
General Motors Corporation	76.7	73.3	56.8	61.1	90.7	72.8	65.8	80.9	80.5	75.2	73.4	21.4	99.5	80.0	73.3	72.1
Standard Oil Development	86.0	79.0	62.0	72.0	97.0	72.0	70.0	87.0	80.0	78.0	75.0	20.0	100.3*	79.0	67.0	74.9
The Texas Company	79.0	74.0	58.0	67.2	90.1	74.4	66.7	83.2	81.0	75.2	71.3	22.9	100.0	73.9	73.0	72.7
Socony-Vacuum Corporation	80.0	75.0	60.0	66.0	88.0	70.0	66.0	82.0	78.0	72.0	72.0	22.0	96.0	77.0	72.0	71.7
Tide Water Oil Company	82.0	71.0	61.0	68.5	87.0	70.0	68.0	83.5	82.0	74.5	72.5	24.5	100.0	72.0	72.5	72.6
Continental Oil Company	78.0	71.0	59.0	65.0	87.0	71.0	66.0	81.0	84.0	74.0	71.0	22.0	95.0	75.0	71.0	71.4
Shell Petroleum Company	80.0	75.5	59.0	70.0	89.5	72.5	67.5	85.0	83.0	75.5	74.0	26.5	96.5	77.5	67.0	73.3
Average	81.3	75.7	61.1	68.2	92.2	73.0	68.6	84.4	82.6	76.0	73.5	22.5	100.0	77.3	71.8	73.9
Standard of California	85.0	77.3	65.0	71.9	91.9	75.8	69.9	87.9	83.0	77.6	73.1	23.0	96.2	80.0	72.7	76.0

*Extrapolated values.



tivity of the two groups previously enumerated, it can be seen that average correlation of the research group would result at a jacket temperature of 237° F., while the branded group would require 340° F. This great difference between these two groups is one of the surprising and unaccountable results of the 1934 Uniontown Hill test, since, as far as is known, there is not enough difference in the composition of the various fuels in these two groups to cause a difference of this sort.

An attempt has been made to explain this difference on the ground that the branded group may have contained some natural gasoline, which would have boiled off in the carburetors, so that the engines would have been supplied with fuels of lower anti-knock than the original products. Examination of the distillation data of these gasolines reveals that the average initial points of the two groups are within 1° F. of each other, and of average 10 percent points are still closer. Even the average Reid vapor pressures are within 0.1 pounds. Thus, this explanation, while apparently reasonable, has to be discarded.

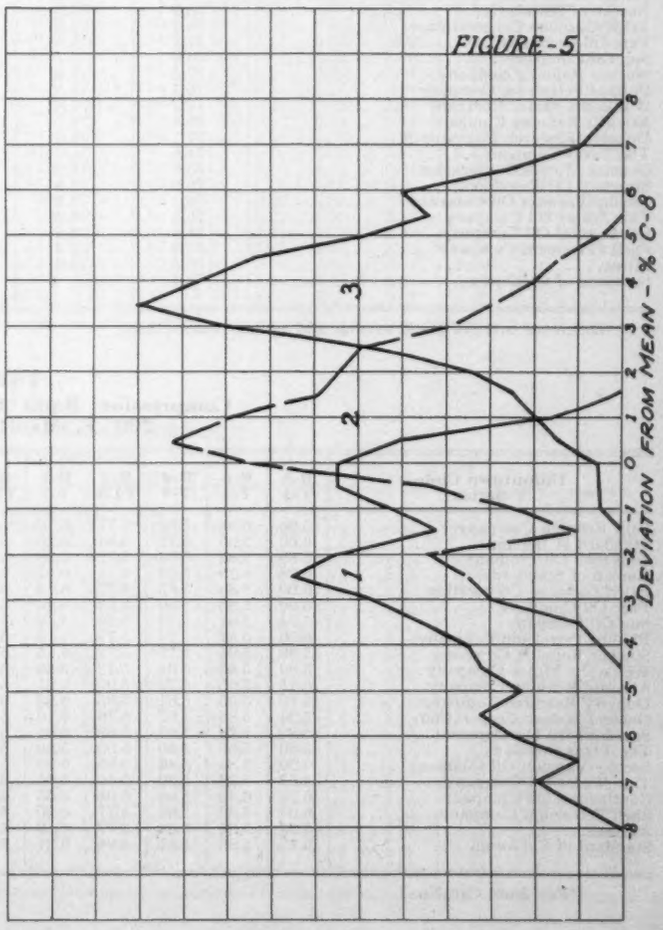
LABORATORY DEVIATIONS

The large amount of data necessitated in this investigation gave an excellent means for investigating the reproducibility of anti-knock readings on the C. F. R. engine in various laboratories, as well as the agreement of various laboratories with each other. Figure 2 has been plotted from the data of Table 6, showing averages of all fuels at each manifold temperature for each laboratory. Column 7 (Table 6) shows the grand average for each laboratory of all fuels at all five temperatures.

The "relative level" of values from each laboratory is indicated in Column 8, as the difference between the grand averages and their mean, and is illustrated in Figure 3A. It can be seen that this range of "relative levels" varies from +3 percent C-8 for the Gulf Refining Company to —1.7 percent C-8 for Shell Petroleum Corporation—a range of almost 1½ octane numbers; and it is probably not due to observational errors, but to some fixed condition of the engine or instrumentation.

With this attempt to separate instrumental from observational errors, the next step is to develop an index for the observational errors. This has been done in Column 9 of Table 6 by totaling for each laboratory, the differences at each temperature (regardless of sign) which remain after deducting the "relative level" from the deviations between the average at each temperature and the mean of all the laboratories at those temperatures. This rather complex expression may be explained graphically by consideration of a chart on which anti-knock values are plotted against manifold temperatures. The total observational deviation is determined by totaling the individual deviations, at each of the five temperatures, from a straight line parallel to the mean of all the laboratories, but a distance from it represented by the "relative level" of that laboratory.

Since each value for any one manifold temperature is the average of 15 fuels, a large step has already been taken in "fairing out" accidental errors. Such relative uniformity is illustrated in Figure 3B, where the relative standing of the various laboratories is seen to be very different from that of Figure 3A. The



best laboratory in this respect has less than one-fifth as great a total deviation as the least "uniform."

Another and more thorough way to analyze the deviations of individual laboratories, but one which is more laborious, is to plot "probability curves," as indicated in Figure 5, for three laboratories. Such curves were made by determining the deviation of every fuel reading, from the average of all laboratories for that fuel and manifold temperature, and then plotting the number of deviations which occurred between 0 and 1 percent C-8, then between 1 and 2 percent, 2 and 3 percent, etc. The sharpness

TABLE 5
Anti-Knock Rating in Terms of Per Cent C-8 in A-3
At 300° F. Mixture Temperature

Uniontown Code T-Series	B-5 T-3	B-6 T-4	B-4 T-5	B-3 TT-6	B-7 T-7	B-8 TT-8	B-2 T-9	B-1 T-10	B-9 T-11	6 T-12	13 T-13	14 T-15	3 T-16	16 T-17	1 T-18	Average
Gulf Refining Company	80.8	75.2	64.4	69.1	94.0	74.7	70.1	87.6	85.7	76.1	73.3	20.3	100.0	77.5	74.4	74.8
Standard of Indiana	82.5	75.5	60.3	68.0	92.2	70.5	67.5	86.2	86.0	76.6	74.5	21.2	98.8	77.5	74.7	74.2
Universal Oil Products	85.0	77.0	64.0	69.0	92.0	72.0	71.0	86.0	85.0	77.0	71.0	22.0	100.0	77.0	73.0	74.7
Bureau of Standards	76.3	73.0	57.8	63.2	87.8	71.7	65.1	78.1	81.6	74.4	72.1	21.2	97.0	76.9	71.4	71.2
Ethyl Gasoline Corporation	77.0	73.0	58.0	65.0	90.0	68.0	64.0	81.0	82.0	73.0	70.0	21.0	96.0	73.0	73.0	71.0
Pure Oil Company	77.5	72.2	58.6	62.5	90.5	72.5	65.0	77.5	83.2	74.9	71.8	20.3	99.2	74.3	65.5	71.0
Sun Oil Company	79.5	75.0	59.0	64.3	91.9	68.5	64.3	82.7	82.0	75.6	71.9	20.5	100.0	77.3	65.8	71.9
Phillips Petroleum Company	78.3	73.0	60.8	65.5	88.8	70.5	66.0	80.0	83.8	75.0	72.0	23.1	95.8	75.5	72.5	72.1
Sinclair Refining Company	76.6	73.5	59.5	62.2	89.0	70.0	64.3	78.5	81.5	72.8	71.2	23.7	94.0	74.4	68.0	70.6
Waukesha Motor Company	76.3	70.0	56.7	63.7	87.5	67.4	63.2	79.6	82.5	72.4	68.6	21.5	94.0	72.6	69.1	69.7
Atlantic Refining Company	77.0	70.0	58.0	68.0	88.0	70.0	65.0	77.0	80.0	72.0	71.0	20.0	95.0	76.0	65.0	70.2
Doherty Research Company	73.5	67.0	55.0	63.0	85.0	71.0	61.0	79.0	79.0	71.5	68.0	20.0	93.0	72.0	65.0	68.2
General Motors Corporation	74.7	70.5	53.6	60.0	86.0	68.1	60.8	79.0	81.1	73.1	71.4	19.4	95.3	73.5	71.7	69.2
Standard Oil Development	79.0	66.0	55.0	62.0	86.0	70.0	61.0	80.0	83.0	70.0	71.0	15.0	92.0	71.0	64.0	68.3
The Texas Company	75.8	71.0	55.9	63.2	87.0	70.8	63.2	80.0	81.0	72.5	68.8	21.2	98.1	73.0	69.5	70.1
Socony-Vacuum Corporation	78.0	74.0	60.0	69.0	87.0	70.0	67.0	84.0	80.0	76.0	68.0	24.0	94.0	76.0	71.0	71.8
Tide Water Oil Company	77.5	69.0	55.0	64.0	86.5	67.5	62.5	79.0	82.0	71.0	67.0	23.0	93.5	70.0	70.0	69.2
Continental Oil Company	74.0	71.0	55.0	62.5	85.0	71.0	65.0	78.0	83.0	71.0	68.0	19.0	94.0	71.0	72.0	69.3
Shell Petroleum Company	70.0	66.0	52.0	61.5	81.0	70.0	61.0	74.5	81.5	68.0	64.5	21.0	92.5	71.0	62.5	66.5
Average	77.3	71.7	57.8	64.5	88.2	70.2	64.6	80.4	82.3	73.3	70.2	20.9	95.9	74.2	69.4	70.7
Standard of California	79.5	72.2	60.0	66.1	88.4	72.2	66.4	80.6	82.4	73.7	70.2	20.0	95.0	74.9	68.9* 75.5†	

*No. 1 can. †No. 2 can.

TABLE 6
Average of All Fuels (In % C-8)

LABORATORY	MANIFOLD TEMPERATURES					Grand Average	*"Laboratory Level"	Total Deviation from Own Level
	200 °F.	225 °F.	250 °F.	275 °F.	300 °F.			
Column Number (1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
Gulf Refining Company	79.2	78.7	77.7	76.4	74.8	77.36	3.75	2.0
Standard of Indiana	77.8	76.9	76.6	74.8	74.2	76.06	2.45	3.0
Universal Oil Products	76.5	76.2	76.5	75.5	74.7	75.88	2.25	6.4
Bureau of Standards	78.2	76.3	74.4	73.1	71.2	74.64	1.03	2.2
Ethyl Gasoline Corporation	78.2	74.6	74.6	72.4	71.0	74.16	0.55	2.6
Pure Oil Company	77.2	75.8	74.3	72.5	71.0	74.16	0.55	1.2
Sun Oil Company	76.0	75.7	74.0	73.0	71.9	74.12	0.51	2.9
Sinclair Refining company	77.2	75.4	73.6	71.7	70.6	73.70	0.09	2.2
Phillips Petroleum Company	75.5	74.5	73.5	72.8	72.1	73.68	0.07	3.9
Waukesha Motor Company	77.3	74.8	73.4	71.1	69.7	73.26	—0.35	3.0
Atlantic Refining Company	75.5	74.7	73.1	71.8	70.2	73.06	—0.55	1.4
Doherty Research Company	77.1	74.6	73.2	70.2	68.2	72.66	—0.95	5.0
The Texas Company	74.6	74.0	72.7	71.7	70.1	72.62	—0.99	2.3
General Motors Corporation	75.6	74.2	72.1	71.8	69.2	72.58	—1.03	2.5
Standard Oil Development	76.0	72.4	74.9	71.3	68.3	72.58	—1.03	5.5
Socony-Vacuum Oil Company	76.1	72.2	71.7	70.7	71.8	72.50	—1.11	5.8
Tide Water Oil Company	76.5	73.2	72.6	69.5	69.2	72.20	—1.41	3.0
Continental Oil Company	74.4	73.5	71.4	70.5	69.3	71.82	—1.79	2.1
Shell Petroleum Company	75.2	73.6	73.3	69.0	66.5	71.52	—2.09	6.3
Mean	76.5	74.8	73.9	72.1	70.7	73.61	....	....
Standard of California	79.4	....	76.0	....	72.2	75.70	2.09	4.7

*Difference between grand average and average mean (73.61).

TABLE 7
Compression Ratio for Anti-Knock Ratings
200° F. Manifold Temperature

Uniontown Code T-Series	B-5 T-3	B-6 T-4	B-4 T-5	B-3 TT-6	B-7 T-7	B-8 TT-8	B-2 T-9	B-1 T-10	B-9 T-11	6 T-12	13 T-13	14 T-15	3 T-16	16 T-17	1 T-18	Average
Gulf Refining Company	5.96	5.92	5.67	5.77	6.16	5.96	5.87	6.07	5.92	5.92	5.89	5.34	6.29	5.97	5.97	5.91
Standard of Indiana	6.00	5.96	5.77	5.84	6.20	5.84	5.80	6.13	6.07	5.88	5.88	5.34	6.38	5.92	5.92	5.92
Universal Oil Products	5.89	5.83	5.64	5.72	5.98	5.70	5.83	5.91	5.88	5.80	5.73	5.30	6.12	5.80	5.73	5.79
Bureau of Standards	6.28	6.16	5.92	6.16	6.47	6.28	6.16	6.28	6.28	6.16	6.16	5.60	6.66	6.16	6.16	6.19
Ethyl Gasoline Corporation	6.00	5.89	5.65	5.77	6.15	5.89	5.78	6.05	5.94	5.89	5.87	5.30	6.20	5.88	5.85	5.87
Pure Oil Company	5.90	5.85	5.50	5.63	6.20	5.82	5.73	6.13	5.97	5.87	5.84	5.31	6.23	5.80	5.72	5.83
Sun Oil Company	5.74	5.62	5.49	5.59	5.79	5.60	5.54	5.70	5.70	5.60	5.60	5.20	5.80	5.60	5.54	5.60
Phillips Petroleum Company	6.00	5.87	5.71	5.77	6.18	5.94	5.79	6.00	6.00	5.87	5.87	5.32	6.18	5.95	5.87	5.88
Sinclair Refining Company	5.96	5.91	5.72	5.72	6.15	5.80	5.81	6.10	5.96	5.91	5.86	5.38	6.26	5.94	5.72	5.88
Waukesha Motor Company	5.89	5.83	5.64	5.72	5.98	5.70	5.83	5.91	5.88	5.80	5.73	5.30	6.12	5.80	5.73	5.79
Atlantic Refining Company	6.15	5.95	5.70	5.90	6.21	5.90	5.95	6.15	6.15	6.00	5.95	5.23	6.35	6.15	5.95	5.98
Doherty Research Company	6.10	5.95	5.81	5.95	6.30	6.08	5.93	6.15	6.00	5.91	5.85	5.30	6.20	5.90	5.85	5.95
General Motors Corporation	5.94	5.85	5.67	5.76	6.10	5.85	5.76	6.01	6.01	5.94	5.85	5.30	6.26	5.80	5.85	5.86
Standard Oil Development	5.82	5.70	5.62	5.69	6.01	5.82	5.69	5.88	5.94	5.94	5.74	5.26	6.20	5.82	5.79	5.79
The Texas Company	5.60	5.60	5.50	5.50	5.80	5.63	5.50	5.80	5.60	5.60	5.60	5.20	5.80	5.60	5.60	5.60
Socony-Vacuum Oil Company	6.00	5.84	5.46	5.80	6.20	5.80	5.80	6.07	6.00	5.88	5.80	5.17	6.31	5.84	5.80	5.84
Tide Water Oil Company	5.53	5.38	5.20	5.40	5.65	5.38	5.30	5.65	5.57	5.47	5.37	4.89	5.94	5.51	5.43	5.44
Continental Oil Company	6.24	6.10	5.90	6.05	6.55	6.05	6.05	6.36	6.30	6.15	6.07	5.55	6.65	6.15	6.07	6.15
Shell Petroleum Company	6.03	5.89	5.68	5.77	6.20	5.83	5.71	6.11	5.96	5.88	5.86	5.25	6.32	5.87	5.76	5.87
Average	5.95	5.85	5.64	5.77	6.12	5.84	5.78	6.03	5.95	5.87	5.82	5.29	6.22	5.87	5.81	5.85
Standard of California	6.15	5.86	5.81	5.94	6.31	5.85	5.90	6.27	6.11	5.85	5.78	5.36	6.45	5.89	5.82*	5.96

*Fuel from Can No. 1.

and height of such curves indicate the "uniformity" of a laboratory, while the distance of the peak from zero deviation indicates approximately the relative "level" of data submitted by that laboratory.

It is assumed that analyzing deviations in this manner might be an aid in locating their causes. An engine and operator, giving non-uniform or inconsistent results, but with a grand average equal to all laboratories, might require a different treatment than one giving consistent but high values.

Finally, in Figure 4 is shown the average deviation (regardless of sign) for all laboratories from the mean for all fuels, as it is affected by manifold temperature. It will be seen that the deviation decreases

TABLE 8

Compression Ratio for Anti-Knock Ratings
225° F. Manifold Temperature

Uniontown Code T-Series	B-5 T-3	B-6 T-4	B-4 T-5	B-3 TT-6	B-7 T-7	B-8 TT-8	B-2 T-9	B-1 T-10	B-9 T-11	6 T-12	13 T-13	14 T-15	3 T-16	16 T-17	1 T-18	Average
Gulf Refining Company	5.86	5.77	5.54	5.57	5.97	5.74	5.67	5.86	5.82	5.72	5.72	5.18	6.05	5.68	5.64	5.72
Standard of Indiana	5.96	5.88	5.70	5.77	6.16	5.77	5.77	6.08	6.00	5.84	5.84	5.28	6.24	5.84	5.81	5.86
Universal Oil Products	5.85	5.75	5.52	5.66	5.93	5.61	5.70	5.88	5.82	5.75	5.61	5.18	5.96	5.72	5.67	5.71
Bureau of Standards	6.12	6.07	5.88	6.05	6.37	6.11	5.88	6.24	6.24	6.07	6.05	5.47	6.51	6.07	6.07	6.08
Ethyl Gasoline Corporation	5.67	5.56	5.32	5.11	5.70	5.52	5.52	5.67	5.67	5.50	5.45	5.00	5.87	5.68	5.51	5.52
Pure Oil Company	5.78	5.78	5.43	5.52	6.08	5.71	5.62	5.95	5.86	5.80	5.76	5.20	6.12	5.21	5.62	5.69
Sun Oil Company	5.69	5.60	5.49	5.54	5.79	5.59	5.54	5.69	5.70	5.60	5.62	5.15	5.84	5.62	5.54	5.60
Phillips Petroleum Company	5.71	5.58	5.44	5.44	5.97	5.58	5.44	5.76	5.76	5.58	5.58	5.13	5.97	5.58	5.58	5.60
Sinclair Refining Company	5.88	5.79	5.57	5.65	6.07	5.67	5.62	5.89	5.82	5.76	5.71	5.19	6.15	5.80	5.72	5.75
Waukesha Motor Company	6.18	6.01	5.76	5.93	6.36	5.97	5.93	6.26	6.23	6.03	6.03	5.38	6.51	6.06	6.00	6.04
Atlantic Refining Company	5.95	5.83	5.70	5.80	6.12	5.80	5.80	5.95	5.95	5.83	5.80	5.28	6.25	5.90	5.70	5.84
Doherty Research Company	5.87	5.75	5.55	5.65	5.95	5.75	5.77	5.90	5.90	5.75	5.75	5.12	6.00	5.70	5.65	5.74
General Motors Corporation	5.82	5.72	5.55	5.67	6.15	5.72	5.67	5.90	5.90	5.72	5.72	5.25	6.15	5.72	5.72	5.76
Standard Oil Development	5.77	5.65	5.45	5.64	5.99	5.64	5.64	5.84	5.70	5.70	5.60	5.30	6.16	5.70	5.72	5.70
The Texas Company	5.52	5.52	5.38	5.38	5.64	5.52	5.38	5.64	5.52	5.52	5.52	5.06	5.64	5.52	5.52	5.48
Socony-Vacuum Oil Company	5.56	5.50	5.25	5.34	5.70	5.43	5.40	5.62	5.56	5.50	5.46	5.04	5.84	5.50	5.50	5.48
Tide Water Oil Company	5.39	5.28	5.14	5.26	5.60	5.30	5.24	5.37	5.38	5.26	5.28	4.83	5.63	5.25	5.27	5.30
Continental Oil Company	6.12	5.97	5.67	5.80	6.25	5.90	5.80	6.20	6.12	6.02	5.90	5.30	6.25	5.90	5.90	5.94
Shell Petroleum Company	5.82	5.68	5.57	5.62	5.94	5.68	5.60	5.87	5.80	5.78	5.76	5.16	6.02	5.72	5.65	5.71
Average	5.82	5.72	5.52	5.60	5.99	5.68	5.63	5.87	5.83	5.72	5.69	5.18	6.06	5.70	5.68	5.71

TABLE 9

Compression Ratio for Anti-Knock Ratings
250° F. Manifold Temperature

Uniontown Code T-Series	B-5 T-3	B-6 T-4	B-4 T-5	B-3 TT-6	B-7 T-7	B-8 TT-8	B-2 T-9	B-1 T-10	B-9 T-11	6 T-12	13 T-13	14 T-15	3 T-16	16 T-17	1 T-18	Average
Gulf Refining Company	5.88	5.72	5.42	5.52	5.92	5.53	5.53	5.86	5.86	5.64	5.64	5.14	6.09	5.73	5.61	5.67
Standard of Indiana	5.89	5.81	5.67	5.70	6.08	5.74	5.77	5.97	5.93	5.85	5.81	5.22	6.28	5.81	5.81	5.82
Universal Oil Products	5.66	5.63	5.43	5.56	5.78	5.55	5.58	5.72	5.72	5.66	5.55	5.07	5.95	5.59	5.52	5.60
Bureau of Standards	5.96	5.88	5.63	5.96	6.16	5.96	5.66	5.96	5.96	5.92	5.92	5.35	6.24	5.92	5.85	5.88
Ethyl Gasoline Corporation	5.75	5.68	5.50	5.48	5.86	5.56	5.48	5.78	5.64	5.64	5.57	5.00	5.92	5.64	5.57	5.60
Pure Oil Company	5.66	5.67	5.36	5.43	5.95	5.63	5.50	5.80	5.71	5.71	5.67	5.09	5.96	5.62	5.53	5.62
Sun Oil Company	5.64	5.54	5.46	5.50	5.79	5.54	5.50	5.64	5.64	5.56	5.54	5.09	5.84	5.59	5.50	5.56
Phillips Petroleum Company	5.65	5.53	5.43	5.54	5.88	5.64	5.49	5.71	5.74	5.61	5.58	5.12	5.94	5.61	5.58	5.60
Sinclair Refining Company	5.69	5.64	5.47	5.52	5.87	5.57	5.57	5.77	5.25	5.66	5.62	5.07	5.94	5.67	5.62	5.59
Waukesha Motor Company	6.01	5.91	5.61	5.77	6.21	5.85	5.77	6.13	6.16	5.99	5.92	5.34	6.39	5.96	5.91	5.97
Atlantic Refining Company	5.75	5.70	5.53	5.68	5.95	5.68	5.66	5.66	5.66	5.66	5.66	5.08	5.98	5.66	5.51	5.65
Doherty Research Company	5.75	5.65	5.47	5.57	5.87	5.65	5.54	5.78	5.75	5.59	5.59	5.04	5.91	5.60	5.55	5.62
General Motors Corporation	5.55	5.55	5.36	5.36	5.89	5.61	5.52	5.72	5.72	5.62	5.65	5.11	6.01	5.77	5.69	5.60
Standard Oil Development	5.73	5.54	5.41	5.47	5.78	5.57	5.57	5.73	5.60	5.53	5.53	5.09	6.00	5.60	5.57	5.58
The Texas Company	5.42	5.42	5.15	5.50	5.56	5.43	5.28	5.39	5.39	5.39	5.39	4.87	5.56	5.39	5.39	5.37
Socony-Vacuum Oil Company	5.40	5.33	5.19	5.20	5.53	5.20	5.13	5.44	5.40	5.40	5.20	4.96	5.62	5.33	5.33	5.31
Tide Water Oil Company	5.24	5.20	5.04	5.18	5.26	5.18	5.16	5.39	5.36	5.25	5.20	4.72	5.63	5.23	5.23	5.22
Continental Oil Company	5.90	5.75	5.55	5.70	6.18	5.70	5.55	5.91	5.92	5.90	5.75	5.22	6.22	5.78	5.82	5.79
Shell Petroleum Company	5.74	5.66	5.39	5.55	5.91	5.62	5.53	5.79	5.79	5.66	5.62	5.08	6.02	5.68	5.56	5.64
Average	5.70	5.62	5.42	5.54	5.86	5.59	5.52	5.74	5.70	5.65	5.60	5.08	5.98	5.64	5.59	5.62
Standard of California	5.91	5.76	5.52	5.59	5.99	5.66	5.63	5.90	5.83	5.70	5.66	5.17	6.07	5.67	5.66*	5.71

*Fuel from Can No. 1.

TABLE 10

Compression Ratio for Anti-Knock Ratings
275° F. Manifold Temperature

Uniontown Code T-Series	B-5 T-3	B-6 T-4	B-4 T-5	B-3 TT-6	B-7 T-7	B-8 TT-8	B-2 T-9	B-1 T-10	B-9 T-11	6 T-12	13 T-13	14 T-15	3 T-16	16 T-17	1 T-18	Average
Gulf Refining Company	5.73	5.64	5.50	5.57	5.75	5.54	5.47	5.61	5.61	5.47	5.46	5.00	5.86	5.51	5.41	5.54
Standard of Indiana	5.77	5.67	5.53	5.60	5.92	5.60	5.57	5.81	5.81	5.67	5.70	5.18	6.08	5.70	5.70	5.68
Universal Oil Products	5.81	5.74	5.50	5.47	5.88	5.52	5.60	5.83	5.81	5.66	5.65	5.15	6.00	5.73	5.65	5.66
Bureau of Standards	6.00	5.91	5.59	5.73	6.11	5.91	5.73	5.91	6.11	5.91	5.91	5.29	6.28	6.00	5.88	5.88
Ethyl Gasoline Corporation	5.35	5.45	5.38	5.34	5.54	5.40	5.38	5.50	5.42	5.42	5.38	5.00	5.65	5.30	5.40	5.39
Pure Oil Company	5.53	5.54	5.30	5.37	5.86	5.54	5.38	5.66	5.63	5.60	5.56	5.05	5.89	5.53	5.48	5.52
Sun Oil Company	5.59	5.46	5.30	5.34	5.69	5.46	5.34	5.59	5.59	5.46	5.40	4.88	5.74	5.46	5.34	5.44
Phillips Petroleum Company	5.50	5.54	5.30	5.30	5.62	5.30	5.30	5.50	5.62	5.54	5.54	5.02	5.78	5.54	5.54	5.46
Sinclair Refining Company	5.62	5.52	5.39	5.42	5.76	5.62	5.48	5.71	5.71	5.58	5.55	5.01	5.90	5.57	5.48	5.55
Waukesha Motor Company	5.82	5.72	5.50	5.59	6.03	5.69	5.62	5.91	5.93	5.76	5.70	5.21	6.16	5.80	5.70	5.74
Atlantic Refining Company	5.61	5.58	5.48	5.48	5.90	5.55	5.45	5.61	5.70	5.61	5.58	5.10	5.90	5.61	5.45	5.57
Doherty Research Company	5.57	5.46	5.33	5.50	5.76	5.60	5.46	5.70	5.65	5.51	5.45	5.82	5.80	5.47	5.41	5.50
General Motors Corporat on	5.55	5.52	5.33	5.43	5.75	5.52	5.43	5.61	5.61	5.55	5.52	5.00	5.90	5.55	5.52	5.52
Standard Oil Development	5.62	5.62	5.46	5.48	5.82	5.58	5.57	5.66	5.82	5.53	5.53	5.05	5.85	5.58	5.58	5.58
The Texas Company	5.35	5.35	5.10	5.21	5.45	5.35	5.21	5.35	5.35	5.35	5.35	4.84	5.45	5.35	5.35	5.29
Socony-Vacuum Oil Company	5.34	5.23	5.17	5.20	5.46	5.23	5.17	5.37	5.37	5.23	5.23	4.91	5.56	5.26	5.25	5.26
Tide Water Oil Company	5.23	5.12	4.97	5.08	5.38	5.08	5.11	5.30	5.33	5.20	5.11	4.71	5.44	5.06	5.08	5.15
Continental Oil Company	5.81	5.70	5.51	5.60	5.86	5.65	5.61	5.80	5.80	5.64	5.64	5.02	5.97	5.66	5.64	5.66
Shell Petroleum Company	5.62	5.55	5.32	5.46	5.82	5.48	5.37	5.66	5.69	5.52	5.46	4.94	4.87	5.52	5.42	5.51
Average	5.60	5.54	5.37	5.43	5.70	5.51	5.44	5.64	5.66	5.54	5.51	5.01	5.85	5.54	5.49	5.52

consistently as the manifold temperature is reduced, the deviation at 200° F. being about 60 percent of that at 300° F.

COMPRESSION RATIOS

The compression ratios at which all anti-knock readings were taken are listed in Tables 7 to 11, inclusive. An analysis of these data has been made in an attempt to correlate the "relative levels" of various laboratories with the average compression ratios used, but without success. While the grand average of the compression ratios used by each laboratory varied from 5.24 to 5.96:1, there appeared to be no relation between the compression ration used by a laboratory and its "relative level" in regard to anti-knock data.

It was interesting to note that the average compression ratio used by all laboratories for each fuel varied consistently with the anti-knock value of the fuel, as shown in Figure 6, for three of the manifold temperatures.

CONCLUSIONS

The following conclusions are based on the assumption that the effect of temperature on the anti-knock values of the gasolines at the time of these tests was the same as at the time of the Uniontown tests.

1. Anti-knock values increase directly with decrease of the manifold temperature.

2. Manifold temperatures of 300° F. or 260° F. would result in equally satisfactory average correlations with the Uniontown Hill data, intermediate temperatures giving better correlations. At about 280° F. all the fuels with negative deviations would exactly cancel the fuels having positive deviations.

3. Dividing the fuels into groups, representing branded commercial fuels and research fuels of known composition and somewhat similar characteristics to the other, indicates temperatures of 340° F. and 237° F., respectively, for similar average correlation.

4. The reproducibility of laboratory data increases with lowering the manifold temperature.

5. Individual anti-knock readings may deviate as much as two octane numbers from the average of all laboratories; although the average of a group of fuels, such as the 15 under consideration in this report, will be within about one octane unit or better.

RECOMMENDATIONS

While the conclusions indicated above seem to suggest the desirability of reducing the manifold temperature of the A. S. T. M. Method, the large and unexplained differences in correlation between the branded and the research groups of fuels throws sufficient question into the results for us to feel doubtful of the magnitude of the desired change. Consequently, we make no recommendation for a change in manifold temperature at this time.

TABLE 11
Compression Ratio for Anti-Knock Ratings
300° F. Manifold Temperature

Uniontown Code T-Series	B-5 T-3	B-6 T-4	B-4 T-5	B-3 TT-6	B-7 T-7	B-8 TT-8	B-2 T-9	B-1 T-10	B-9 T-11	6 T-12	13 T-13	14 T-15	3 T-16	16 T-17	1 T-18	Average	Grand Average†
Gulf Refining Company	5.53	5.53	5.34	5.42	5.78	5.53	5.41	5.64	5.61	5.47	5.47	4.96	5.97	5.47	5.47	5.51	5.67
Standard of Indiana	5.70	5.64	5.47	5.50	5.88	5.56	5.53	5.73	5 73	5.64	5.64	5.10	6.00	5.64	5.64	5.62	5.78
Universal Oil Products	5.61	5.52	5.34	5.38	5.70	5.47	5.43	5.64	5.61	5.52	5.44	4.96	5.83	5.51	5.48	5.50	5.65
Bureau of Standards	5.77	5.77	5.56	5.59	5.96	5.77	5.59	5.84	5.96	5.77	5.73	5.26	6.20	5.77	6.73	5.75	5.96
Ethyl Gasoline Corporation	5.52	5.45	5.32	5.38	5.55	5.45	5.38	5.46	5.47	5.45	5.46	5.02	5.73	5.45	5.46	5.44	5.56
Pure Oil Company	5.46	5.43	5.23	5.31	5.74	5.43	5.31	5.50	5.53	5.50	5.48	5.00	5.83	5.42	5.38	5.43	5.62
Sun Oil Company	5.50	5.41	5.26	5.30	5.64	5.36	5.30	5.54	5.54	5.41	5.36	4.75	5.72	5.41	5.30	5.38	5.52
Phillips Petroleum Company	5.41	5.41	5.24	5.29	5.63	5.39	5.24	5.56	5.63	5.46	5.44	4.92	5.79	5.49	5.44	5.42	5.59
Sinclair Refining Company	5.53	5.46	5.26	5.35	5.57	5.39	5.33	5.55	5.55	5.47	5.40	4.93	5.75	5.47	5.41	5.43	5.64
Waukesha Motor Company	5.71	5.63	5.38	5.41	5.81	5.52	5.46	5.77	5.74	5.63	5.53	5.11	5.96	5.65	5.53	5.59	5.93
Atlantic Refining Company	5.50	5.43	5.23	5.45	5.60	5.45	5.30	3.60	5.50	5.50	5.30	4.90	5.80	5.50	5.30	5.42	5.69
Doherty Research Company	5.50	5.41	5.30	5.40	5.71	5.56	5.42	5.58	5.58	5.43	5.36	4.78	5.70	5.40	5.37	5.43	5.65
General Motors Corporation	5.46	5.46	5.22	5.30	5.71	5.36	5.30	5.51	5.51	5.46	5.46	4.93	5.80	5.46	5.43	5.42	5.63
Standard Oil Development	5.49	5.41	5.26	5.38	5.63	5.48	5.37	5.57	5.57	5.50	5.50	4.97	5.76	5.46	5.41	5.45	5.62
The Texas Company	5.26	5.13	5.00	5.17	5.38	5.17	5.13	5.26	5.26	5.13	5.13	4.75	5.38	5.26	5.13	5.17	5.38
Socony-Vacuum Oil Company	5.50	5.43	5.27	5.37	5.66	5.40	5.37	5.66	5.50	5.46	5.37	4.96	5.74	5.44	5.43	5.44	5.47
Tide Water Oil Company	5.16	5.05	4.89	5.00	5.28	5.03	5.01	5.15	5.23	5.08	5.05	4.62	5.38	5.04	5.07	5.07	5.24
Continental Oil Company	5.70	5.55	5.38	5.48	5.85	5.55	5.46	5.76	5.85	5.66	5.55	5.06	6.05	5.66	5.55	5.60	5.83
Shell Petroleum Company	5.46	5.36	5.19	5.37	5.66	5.44	5.33	5.52	5.62	5.41	5.36	4.87	5.76	5.45	5.34	5.41	5.63
Average	5.51	5.45	5.27	5.36	5.67	5.44	5.35	5.57	5.58	5.47	5.42	4.94	5.80	5.47	5.41	5.45	5.63
Standard of California	5.52	5.47	5.28	5.43	5.72	5.46	5.44	5.58	5.69	5.56	5.52	4.96	5.94	5.62	5.46*	5.51	5.72

*Fuel from Can No. 1. †All temperatures.

TABLE 4
Anti-Knock Rating in Terms of Per Cent C-8 in A-3
At 275° F. Mixture Temperature

Uniontown Code T-Series	B-5 T-3	B-6 T-4	B-4 T-5	B-3 TT-6	B-7 T-7	B-8 TT-8	B-2 T-9	B-1 T-10	B-9 T-11	6 T-12	13 T-13	14 T-15	3 T-16	16 T-17	1 T-18	Average
Gulf Refining Company	84.1	78.1	64.2	70.7	94.6	75.0	71.3	88.3	86.0	77.5	74.4	23.4	104.0*	80.4	74.4	76.4
Standard of Indiana	83.2	76.3	60.7	69.0	94.5	71.0	68.4	88.0	84.7	76.8	75.0	21.5	100.0	78.6	75.8	74.8
Universal Oil Products	85.0	79.0	62.0	70.0	95.0	72.0	72.0	87.0	85.0	77.0	74.0	22.0	101.0*	79.0	74.0	75.5
Bureau of Standards	76.9	75.1	59.3	67.6	89.6	74.5	66.1	79.8	86.3	75.9	72.4	22.5	97.9	78.2	74.0	73.1
Ethyl Gasoline Corporation	83.0	72.0	59.0	67.0	92.0	69.0	67.0	83.0	83.0	73.0	72.0	21.0	98.0	74.0	73.0	72.4
Pure Oil Company	79.5	74.3	60.4	63.7	92.1	73.5	66.2	80.2	83.4	76.3	73.0	21.0	100.5*	75.8	67.5	72.5
Sun Oil Company	82.5	75.2	60.5	65.3	93.2	71.2	65.3	84.1	82.5	76.7	73.6	20.5	100.5*	77.0	67.3	73.0
Phillips Petroleum Company	79.5	74.0	60.0	66.5	89.5	70.0	67.0	82.0	84.0	76.0	73.0	23.0	97.5	76.5	72.5	72.8
Sinclair Refining Company	77.7	75.0	60.5	64.0	90.0	70.5	65.3	81.0	81.7	73.6	71.8	24.3	95.5	76.0	68.3	71.7
Waukesha Motor Company	77.9	71.7	58.0	64.6	90.0	70.0	65.0	82.7	83.5	72.4	69.6	21.4	95.4	73.6	70.0	71.1
Atlantic Refining Company	79.0	72.0	60.0	70.0	90.0	72.0	66.0	80.0	81.0	75.0	72.0	20.0	98.0	77.0	66.0	71.8
Doherty Research Company	76.5	68.5	57.0	63.5	87.0	72.0	64.5	82.0	79.5	71.5	70.5	20.0	98.0	73.5	68.0	70.2
General Motors Corporation	77.8	77.1	56.5	63.8	90.0	72.2	65.1	80.5	81.8	75.5	72.0	20.7	96.1	75.0	72.5	71.8
Standard Oil Development	79.0	69.0	57.0	66.0	87.0	71.0	67.0	83.0	82.0	75.0	71.0	20.0	97.0	74.0	72.0	71.3
The Texas Company	78.1	72.0	57.1	64.5	88.8	72.1	65.3	82.5	81.9	74.5	71.9	22.0	99.2	73.2	72.0	71.7
Socony-Vacuum Corporation	79.0	71.0	58.0	66.0	88.0	69.0	65.0	80.0	81.0	75.0	70.0	19.0	94.0	74.0	71.0	70.7
Tide Water Oil Company	76.5	68.5	54.0	64.5	85.5	68.5	64.0	80.5	83.0	72.0	67.5	23.0	95.5	70.0	70.5	69.5
Continental Oil Company	77.5	71.0	56.5	64.0	87.0	71.0	65.5	80.0	83.0	73.0	68.0	20.5	95.5	74.5	70.0	70.5
Shell Petroleum Company	72.5	68.0	55.5	65.5	85.5	71.5	63.0	78.5	81.5	72.0	68.0	22.0	93.5	73.0	65.0	69.0
Average	79.3	73.0	59.8	66.1	90.0	71.4	66.3	82.2	82.9	74.7	71.6	21.5	97.8	75.4	70.7	72.1

*Extrapolated values.

Polymer Gasoline from Cracked Gases

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and
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A COMMERCIAL polymerization unit recently put into operation is processing 3,000,000 cubic feet a day of cracked gas, and producing about five gallons of polymer gasoline per 1000 cubic feet. This gasoline has an octane rating of 80-82 "motor method," and its blending value is higher than that of benzene or *iso*octane.

The process is that developed by Universal Oil Products Company, and reported at the recent New York meeting of the American Chemical Society.

The unit is operating under mild conditions of temperature and pressure, using a solid catalyst. The stabilizer gas being processed contains about 29 percent of propylene and butylenes.

Cracked gases are made up of paraffin hydrocarbons, and also members of the olefinic series—including ethylene, propylene, and butylenes. These olefins react at relatively low temperatures and pressures in the presence of the solid catalyst to produce polymer gasoline.

The following data were obtained from the operation of two pilot polymerization plants of 400- and 85,000-cubic foot daily capacity.

POLYMERIZATION OF STABILIZER GAS OBTAINED FROM REFORMING MID-CONTINENT STRAIGHT-RUN GASOLINE

A continuous 22-day run was made in a semi-commercial polymerizing plant. The operating conditions were about 3500 cubic feet of gas per hour, temperature 475° F., and 160 pounds gage, pressure. The gas being processed was passed through a heating coil under the stabilizer pressure of 160 pounds, and delivered into the three insulated catalyst chambers connected in series flow.

In the first part of the run the hydrogen sulfide (0.8 percent by volume) was not removed from the stabilizer gas, and part of it appeared in the polymer gasoline as sulfur compounds, mostly mercaptans, due to the interaction of hydrogen sulfide with the olefins present in the gas. In the second part of the run the hydrogen sulfide was removed from the stabilizer gas before polymerization by scrubbing with 23° Beaume caustic soda solution.

The sulfur present in the polymer gasoline is a function of the hydrogen sulfide content of the gas being processed. With caustic-scrubbed gas, the sulfur content of the liquid polymer approaches zero. In the present run the polymer gasoline produced from the unscrubbed gas contained 0.63 percent of sulfur (76 percent of which was mercaptans); whereas the gasoline from the scrubbed gas was doctor-sweet, and contained only 0.02 percent of sulfur.

The compositions of the inlet gas to the process and of the outgoing gas are presented in Table 1, the values being obtained by low temperature Podbielniak distillation. Hydrogen sulfide was removed from the gas before distillation. Columns 1 and 2 list the actual analytical figures of the inlet and outlet gases, whereas column 3 has been corrected for the shrinkage of the gas due to polymerization. Columns 1 and 3, therefore, represent the relative volumes of the various components of the ingoing and outgoing gases; i. e., for every 100 cubic feet of inlet gas there were 74.7 cubic feet of outlet gas. The routine analytical method used in plant control consisted in the absorption of propylene and butylenes by means of 87 percent sulfuric acid.

TABLE 1

Analyses of Inlet and Outlet Gases

GAS	Inlet Gas (Percent)	Outlet Gas (Percent)	Outlet Gas ×0.747 (Percent)
Non-condensibles	5.5	2.4	1.8
Ethylene	2.9	5.0	3.7
Ethane	13.4	33.9	25.2
Propylene	15.3	4.9	3.7
Propane	39.4	37.6	28.2
*Iso*butylene	3.8	0.3	0.2
n-Butylenes	5.9	1.4	1.1
Butanes	12.9	14.5	10.8
Pentanes and higher	0.9	0.0	0.0
Totals	100.0	100.0	74.7

POLYMERIZATION OF STABILIZER GAS CONTAINING HYDROGEN SULFIDE

Run data obtained with unscrubbed stabilizer gas (containing 0.8 percent of hydrogen sulfide) are presented in the left column of Table 2, which shows the operating conditions, the olefin content of the gas, the extent of olefin polymerization, and the yield of liquid polymer.

Distillation and other characteristics of the crude liquid polymer as produced are presented in the left column of Table 3.

POLYMERIZATION OF STABILIZER GAS FREE FROM HYDROGEN SULFIDE

The stabilizer gas containing 0.8 percent of hydrogen sulfide was passed from the stabilizer of the reforming unit through a 23 Beaume caustic soda solution at 150° F. This treatment reduced the hydrogen sulfide to less than 0.01 percent., Data from this part of the 22-day run are shown in the right column of Table 2.

Distillation and other characteristics of the crude liquid polymer as produced are presented in the right column of Table 3.

POLYMERIZATION OF GAS OBTAINED FROM "VAPOR-PHASE" CRACKING OF MEXICAN GAS OIL

In the vapor-phase cracking of Mexican gas oil, gases containing various percentages of olefins are

TABLE 2

Polymerization of Stabilizer Gas

	Unscrubbed Gas	Scrubbed Gas
Operating Conditions:		
Hours on test	444	93
Gage pressure, lb. per sq. in.	160	160
Temperature, ° F.	475	475
Inlet-gas rate, cu. ft. per hour	3,430	3,520
Outlet-gas rate, cu. ft. per hour	2,566	2,617
Higher Olefin Content of Inlet Gas:		
Propylene and butylenes, percent	26.2	24.4
Higher Olefin Content of Outlet Gas:		
Propylene and butylenes, percent	8.3	9.7
Olefin Polymerization:		
Propylene and butylenes, percent	76	71
Liquid Polymer Production:		
Gallons per 1,000 cu. ft.	4.7	3.6

TABLE 3

Crude Liquid Polymer

	Unscrubbed Gas	Scrubbed Gas
API gravity at 60° F.	69.5	67.2
Gum, mg. per 100 cc. (copper dish)	23	51
Gum, mg. per 100 cc. (air jet)	16	10
Percent sulfur, total	0.63	0.02
Percent sulfur, mercaptan	0.48	0.0
Octane No. (C.F.R. motor method)	82	82
Induction period, min.	90	45
Reid vapor pressure at 100° F., lb.	12.8	10.6
	(Deg. F.)	(Deg. F.)
ASTM Distillation:		
Initial boiling point	89	94
10 percent point	140	158
20 percent point	169	186
30 percent point	192	199
40 percent point	204	207
50 percent point	214	215
60 percent point	227	224
70 percent point	245	241
80 percent point	289	277
90 percent point	355	333
End point	415	415
Total percent over	95	95
Percent bottoms	1	1
Percent loss	4	4

TABLE 4

Analyses of Inlet and Outlet Gases

GAS	(1) Inlet Gas (Percent)	(2) Outlet Gas (Percent)	(3) Outlet Gas ×0.787 (Percent)
Non-condensibles	19.8	26.4	20.8
Ethylene	14.9	17.5	13.8
Ethane	19.8	26.5	20.8
Propylene	19.4	7.2	5.7
Propane	18.2	19.4	15.2
*Iso*butylene	1.8	0.0	0.0
n-Butylenes	3.8	0.0	0.0
Butanes	1.5	3.0	2.4
Pentanes and higher	0.8	0.0	0.0
Totals	100.0	100.0	78.7

TABLE 5

Run Data

TEST NO.	(1)	(2)
Operating Conditions:		
Hours on test	60	264
Gage pressure, lb. per sq. in.	175	175
Temperature, ° F.	450	500
Inlet-gas rate, cu. ft. per hour per lb.	3.9	5.6
Higher Olefin Content of Inlet Gas:		
Propylene and butylenes, percent	26.3	27.2
Higher Olefin Content of Outlet Gas:		
Propylene and butylenes, percent	7.5	4.2
Olefin Polymerization:		
Propylene and butylenes, percent	77	88
Liquid Polymer Production:		
Gallons per 1,000 cu. ft.	3.7	3.8

produced. A blend of the absorption tower and the stabilizer tower gases was made in the proportion in which they were produced in a commercial cracking unit making 6,500,000 cubic feet of gas per day, five volumes of absorption gas to one of stabilizer gas.

The mixed gas was polymerized at 175 pounds, gage, pressure; temperatures of 450 and 500° F., and at feed rates of 3.9 cubic feet and 5.6 cubic feet per hour per pound of catalyst.

Analyses of the inlet and outlet gases are listed in Table 4. Columns 1 and 2 give the actual gas analytical figures, whereas the values in column 3 have been corrected for the change in gas volume due to polymerization; i. e., for 100 cubic feet of inlet gas there were 78.7 cubic feet of outlet gas.

Table 5 presents run data showing the operating conditions, the olefin content of the gas before and after polymerization, and the yield of liquid polymer.

Table 6 presents distillation and other characteristics of the crude liquid polymer as produced.

POLYMERIZATION OF STABILIZER GAS OBTAINED FROM "LIQUID-VAPOR-PHASE" CRACKING OF MID-CONTINENT GAS OIL

The stabilizer gas was processed at 100 pounds and 155 pounds gage pressure, and at 450° F. with varying time factors. The contact times were varied from 24 to 173 seconds. The propylene-butylene content of the gas averaged 35 percent. The liquid polymer production per 1000 cubic feet ranged from 5.6 to 8.4 gallons.

Table 7 presents average gas analytical data for the inlet and outlet gases. Columns 1 and 2 list the actual gas analysis figures, whereas the values in column 3 have been corrected for the change in gas volume due to polymerization.

The processing of the stabilizer gas was continued for eight days, during which time four different sets of operating conditions were tested in order to determine the effect of contact time on the quality of the liquid polymer. The results are shown in Tables 8 and 9.

Table 9 presents distillation and other characteristics of the crude liquid polymer as produced during the four tests.

The boiling range of the polymer product does not affect the octane rating to any extent.

Table 10 presents data from the above runs which show the effect of contact time upon the extent of polymerization, and upon the yield and boiling range of the liquid polymer.

POLYMERIZATION OF PROPANE-PROPYLENE AND BUTANE-BUTYLENE FRACTIONS

In some refineries the stabilizer for producing gasoline of desired vapor pressure is operated so as to yield a propane-propylene and a butane-butylene fraction, or mixtures thereof. These separate fractions and a mixed fraction were studied with the view of producing liquid polymer and substantially olefin-free gas, i. e., propane, butane, or a mixture of propane and butane.

The gases were processed at 450° F. and at 100 pounds pressure, at gas rates of 0.05 to 0.25 cubic feet per hour per pound of catalyst. Under these operating conditions, 92 to 99 percent of the olefin content

TABLE 6
Crude Liquid Polymer

TEST NO.	(1)	(2)
API gravity at 60° F.	59.7	60.2
Sulfur, percent	0.14	0.14
Octane No. (C.F.R. motor method)	80	80
Reid vapor pressure at 100° F., lb.	5.3	5.6
	(Deg. F.)	(Deg. F.)
ASTM Distillation:		
Initial boiling point	135	121
10 percent point	198	188
20 percent point	216	204
30 percent point	229	216
40 percent point	240	228
50 percent point	256	239
60 percent point	274	259
70 percent point	299	286
80 percent point	328	318
90 percent point	390	370
End point	487	476
Total percent over	96.5	97.0
Percent bottoms	1.0	1.5
Percent loss	2.5	1.5

TABLE 7
Analyses of Inlet and Outlet Gases

GAS	(1) Inlet Gas (Percent)	(2) Outlet Gas (Percent)	(3) Outlet Gas ×0.671 (Percent)
Non-condensibles	0.0	0.0	0.0
Ethylene	0.7	1.1	0.7
Ethane	6.1	10.0	6.7
Propylene	18.4	3.5	2.3
Propane	46.3	71.8	48.3
*Iso*butylene	4.4	0.2	0.1
n-Butylenes	10.1	2.4	1.6
Butanes	13.1	9.8	6.6
Pentanes and higher	0.7	1.2	0.8
Hydrogen sulfide	0.2	0.0	0.0
Totals	100.0	100.0	67.1

TABLE 8
Run Data

TEST NO.	(1)	(2)	(3)	(4)
Operating Conditions:				
Hours on test	48	48	48	42
Gage pressure, lbs. per sq. in.	100	155	155	155
Temperature, ° F.	450	450	450	450
Inlet-gas rate, cu. ft. per hour per lb. of catalyst	1.1	4.4	6.7	11.4
Higher Olefin Content of Inlet Gas: Propylene and butylenes, percent	37.5	34.6	34.3	36.0
Higher Olefin Content of Outlet Gas: Propylene and butylenes, percent	0.3	4.0	6.2	10.4
Olefin Polymerization: Propylene and butylenes, percent	99	92	87	79
Liquid Polymer Production: Gallons per 1,000 cu. ft.	8.4	7.4	6.6	5.6

TABLE 9
Crude Liquid Polymer

TEST NO.	(1)	(2)	(3)	(4)
API gravity at 60° F.	62.7	66.4	67.8	66.6
Sulfur, percent	0.12	0.23	0.32	0.31
Octane No. (C.F.R. motor method)	81	80	82	81
Reid vapor pressure at 100° F., lb.	14.0	13.9	14.0	12.5
	(° F.)	(° F.)	(° F.)	(° F.)
ASTM Distillation:				
Initial boiling point	95	89	84	104
10 percent point	158	164	148	166
20 percent point	188	194	182	189
30 percent point	210	209	196	199
40 percent point	235	221	211	206
50 percent point	258	234	222	214
60 percent point	292	254	238	225
70 percent point	327	290	262	244
80 percent point	372	328	310	293
90 percent point	460	420	372	352
End point	531	439	413	411
Total percent over	94.0	91.5	92.0	93.5
Percent bottoms	1.5	1.5	2.0	2.0
Percent loss	4.5	7.0	6.0	4.5

of the gas was removed in the form of liquid polymer.

Analyses of the inlet and outlet gases are given in Table 11. Columns 1 and 2 show the actual gas-analysis figures, whereas the values in column 3 have been corrected for the change in gas volume due to polymerization.

Run data are presented in Table 12—showing the operating conditions, the olefine content of the gases before and after polymerization, the extent of olefin polymerization, and the polymer yields. Each gas was processed at two feed rates.

Distillation and other characteristics of the crude liquid polymer are presented in Table 13.

PROPERTIES OF POLYMER GASOLINE

The outstanding characteristic of polymer gasoline is its high octane number and blending value. The distillation range can vary considerably without affecting its anti-knock qualities, as shown in Table 14.

Polymer gasoline has higher blending value (Table 15) than either benzene or *iso*octane, although its straight octane value is lower—81 versus 97 and 100, respectively. Its blending value becomes higher the lower the octane number of the base fuel with which it is blended.

Tables 16 and 17 list the octane numbers of various blends of steam-distilled polymer gasoline (end point, 390° F.) with straight-run and with reformed gasoline.

Table 18 shows the distillation characteristics of the three gasolines—polymer, straight run, and reformed—used in these blends.

Figures 1 and 2 present graphically the blending characteristics of polymer gasoline at different concentrations in a number of base fuels. The family of curves in Figure 1 makes it possible to predict approximately the octane number that can be expected from blending polymer gasoline with different motor fuels.

The boiling range of the liquid polymer is a function of the operating conditions. By proper choice of the time, temperature, and pressure variables, the distillation range of the liquid polymer can be varied at will. The sulfur content of the polymer gasoline can also be controlled. In case a sulfur-free crude polymer is desired, the gas being processed is freed from hydrogen sulfide before polymerization. This is readily accomplished by a caustic-soda wash.

Crude polymer gasoline has low oxygen bomb stability, but high susceptibility to inhibitor. One hundredth of one per cent (0.01 percent) of wood distillate inhibitor is usually sufficient to produce a gasoline of satisfactory stability.

Table 19 lists the gum, oxygen bomb stability, anti-knock and other characteristics of four typical crude

TABLE 10

Effect of Contact Time on Extent of Polymerization and Yield and Boiling Range of Polymer

TEST NO.	(1)	(2)	(3)	(4)
Contact time, sec.	173	65	42	24
Inlet-gas rate, cu. ft. per hour per lb. of catalyst	1.1	4.4	6.7	11.4
Polymerization of propylene and butylenes, percent	99	92	87	79
Gallons of liquid polymer per 1,000 cu. ft. of gas	8.4	7.4	6.6	5.6
90 percent point, ° F.	460	420	372	352
End point, ° F.	531	439	413	411

polymer gasolines as produced in a semi-commercial plant from stabilizer gas.

REACTIVATION OF THE CATALYST

The solid catalyst gradually loses its activity with continued use, but it is readily regenerated with a controlled volume of air which burns off the highly polymerized or carbonaceous material that deposits upon the catalyst. This reactivation step has been carried out a number of times, each time bringing the catalyst back to its original activity. The 22-day

TABLE 11
Analyses of Inlet and Outlet Gases

GAS	Propane-Propylene Fraction			Butane-Butylene Fraction			Propane-Propylene Butane-Butylene Fraction		
	(1) Inlet Gas (Percent)	(2) Outlet Gas (Percent)	(3) Outlet Gas ×0.828 (Percent)	(1) Inlet Gas (Percent)	(2) Outlet Gas (Percent)	(3) Outlet Gas ×0.604 (Percent)	(1) Inlet Gas (Percent)	(2) Outlet Gas (Percent)	(3) Outlet Gas ×0.620 (Percent)
Non-condensibles	0.8	0.8	0.7	2.2	6.1	3.7	6.7	6.0	3.7
Propylene	28.9	0.0	0.0	4.4	2.0	1.2	10.0	2.2	1.4
Propane	70.3	93.8	77.6	9.1	27.8	16.8	29.4	47.2	29.3
Butylenes	0.0	0.0	0.0	33.6	0.5	0.3	28.0	2.3	1.4
Butanes	0.0	0.0	0.0	50.7	60.2	36.3	25.9	42.3	26.2
Pentanes and higher	0.0	5.4	4.5	0.0	3.4	2.1	0.0	0.0	0.0

TABLE 12

Test No.	Propane-Propylene Fraction (1)	Propane-Propylene Fraction (2)	Butane-Butylene Fraction (3)	Butane-Butylene Fraction (4)	Propane-Propylene Butane-Butylene Fraction (5)	Propane-Propylene Butane-Butylene Fraction (6)
Operating Conditions:						
Hours on test	20	20	20	12	17	22
Gage pressure, lb. per sq. in.	100	100	100	100	100	100
Temperature, °F.	450	450	450	450	450	450
Inlet-gas rate, cu. ft. per hour per lb. of catalyst	0.12	0.05	0.19	0.10	0.25	0.10
Olefin Content of Inlet Gas:						
Propylene and butylenes, percent	26.6	29.3	35.0	41.0	39.6	43.6
Olefin Content of Outlet Gas:						
Propylene and butylenes, percent	2.6	0.4	4.6	0.4	3.4	1.4
Olefin Polymerization:						
Propylene and butylenes, percent	92	99	92	99	95	98
Liquid Polymer Production:						
Gallons per 1,000 cu. ft.	3.8	3.0	8.4	7.2	7.5	7.5

TABLE 13
Crude Liquid Polymer

Test No.	Propane-Propylene Fraction (1)	Propane-Propylene Fraction (2)	Butane-Butylene Fraction (3)	Butane-Butylene Fraction (4)	Propane-Propylene Butane-Butylene Fraction (5)	Propane-Propylene Butane-Butylene Fraction (6)
API gravity at 60 °F.	57.9	59.3	60.5	60.3	62.5	60.2
Sulfur, percent	0.37	...	0.02	...	0.02	0.03
Reid vapor pressure at 100 °F., lb.	...	...	15.6	...	...	16.3
ASTM Distillation:	(Deg. F.)	(Deg. F.)	(Deg. F.)	(Deg. F.)	(Deg. F.)	(Deg. F.)
Initial boiling point	110	104	80	90	84	100
10 percent point	180	148	136	128	116	154
20 percent point	204	172	186	164	156	196
30 percent point	224	194	228	202	198	230
40 percent point	246	216	256	232	230	258
50 percent point	270	250	290	262	258	286
60 percent point	302	286	330	304	294	326
70 percent point	338	330	372	358	350	374
80 percent point	384	374	422	404	420	428
90 percent point	460	431	574	538	570	612
End point	570	516	574	586	602	612

TABLE 14
Anti-knock Characteristics of Polymer Gasoline

API gravity at 60 °F.	62.7	59.9	66.4	67.8	66.6
ASTM Distillation:	(Deg. F.)	(Deg. F.)	(Deg. F.)	(Deg. F.)	(Deg. F.)
Initial boiling point	95	94	89	84	104
10 percent point	158	145	164	148	166
20 percent point	188	181	194	182	189
50 percent point	258	268	234	222	214
90 percent point	460	484	420	372	352
End point	531	510	439	413	411
Octane No. (C.F.R. motor method)	81	81	80	82	81
Octane blending value (25 percent in fuel "A-3" of 44 octane No.; C.F.R. motor method)	118	118	116	120	116

TABLE 15

Octane Blending Value of Polymer Gasoline

(A) POLYMER GASOLINE BLENDS

Percent of Polymer Gasoline in Blend:	(5)	(10)	(15)	(20)	(25)
Octane Blending Value:					
In 45 octane No. base fuel	125	125	121	120	117
In 55 octane No. base fuel	125	120	115	113	111
In 65 octane No. base fuel	105	105	105	105	103

(B) BENZENE BLENDS

Percent of Benzene in Blend:	(5)	(10)	(15)	(20)	(25)
Octane Blending Value:					
In 45 octane No. base fuel	84	85	84	84	86
In 55 octane No. base fuel	84	85	88	90	89
In 65 octane No. base fuel	84	85	88	90	91

(C) *ISO*OCTANE BLENDS

Percent of *Iso*octane in Blend:	(5)	(10)	(15)	(20)	(25)
Octane Blending Value:					
In 45 octane No. base fuel	94	94	94	96	96
In 55 octane No. base fuel	90	91	95	98	99
In 65 octane No. base fuel	90	90	95	97	97

(D) STRAIGHT OCTANE NUMBERS

Polymer gasoline	81
Benzene	97
*Iso*octane	100

TABLE 16

Octane Ratings of Blends of Polymer and Straight-run Gasolines

Polymer gasoline in blend, percent	100	0	5	10	15	25
Straight-run gasoline in blend, percent	0	100	95	90	85	75
Octane No. of blend (C.F.R. motor method)	80	44	48	52	56	62

TABLE 17

Octane Ratings of Blends of Polymer and Reformed Gasolines

Polymer gasoline in blend, percent	100	0	5	10	15	25
Reformed gasoline in blend, percent	0	100	95	90	85	75
Octane No. of blend (C.F.R. motor method)	80	72	73	74	75	76

TABLE 18

Distillation Characteristics of Gasoline Used in Blending

	GASOLINES		
	Polymer (Deg. F.)	Straight-run (Deg. F.)	Reformed (Deg. F.)
ASTM Distillation:			
Initial boiling point	138	142	122
5 percent point	178	174	149
10 percent point	193	190	163
20 percent point	208	207	185
30 percent point	218	220	203
40 percent point	228	237	220
50 percent point	239	249	236
60 percent point	251	255	252
70 percent point	272	266	270
80 percent point	296	283	290
90 percent point	327	304	318
End point	390	360	366

TABLE 19
Crude Polymer

	(1)	(2)	(3)	(4)
API gravity at 60 °F	65.9	68.0	68.1	67.8
Gum, mg. per 100 cc. (copper dish)	15	34	38	44
Gum, mg. per 100 cc. (ASTM)	4	11	6	8
Induction period, min.	35	60	50	45
Induction period +0.01 percent wood distillate inhibitor	....	260	205	305
Induction period +0.025 percent wood distillate inhibitor	235	660	510	595
Induction period +0.05 percent wood distillate inhibitor	430	1,030	835	845
Percent sulfur, total	0.77	0.02	0.02	0.04
Percent sulfur, mercaptan	0.54	0.002	0.007	0.006
Octane No. (C.F.R. motor method)	80	80	81	81
Octane blending value (25 percent in fuel "A-3"; octane No. 44; C.F.R. motor method)	114	116	120	120
Reid vapor pressure at 100 °F., lb.	9.4	10.8	10.5	8.6
ASTM Distillation:	(Deg. F.)	(Deg. F.)	(Deg. F.)	(Deg. F.)
Initial boiling point	115	100	102	107
5 percent point	146	125	148	132
10 percent point	160	143	156	152
20 percent point	184	177	178	180
30 percent point	199	193	196	196
40 percent point	209	203	205	206
50 percent point	219	211	214	212
60 percent point	232	221	222	219
70 percent point	254	236	243	235
80 percent point	294	266	270	261
90 percent point	337	326	336	326
End point	409	418	418	409
Total percent over	94.5	97.0	97.0	97.0
Percent bottoms	1.5	1.4	1.5	1.5
Percent loss	4.0	1.6	1.5	1.5

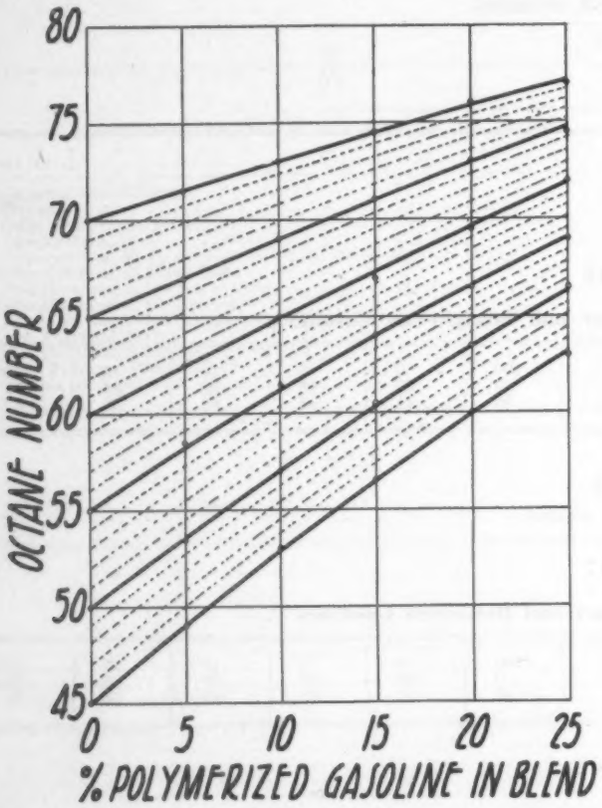

FIGURE 1

Blending Value of Polymerized Gasoline When Blended with Straight-run Gasolines—Blends of Reference Fuels "C-8" and "A-3."

run reported in this paper was made with a catalyst which had been regenerated in the tower used for polymerization.

SUMMARY

Experiments are described concerning the polymerization of five samples of cracked gases in semi-commercial polymerization units. The operating conditions of gas rate, temperature, and pressure varied from 0.05 to 11.4 cubic feet per hour per pound of catalyst, 450 to 500° F., and 100 to 175 pounds per square inch gage, pressure. The yields of liquid polymer ranged from 3.0 to 8.4 gallons per 1000 cubic feet, with olefin polymerizations of 71 to 99 percent.

The outstanding characteristic of polymer gasoline is its high octane number and blending value. Its distillation range can vary considerably without affecting its anti-knock qualities, and it has higher blending value than either benzene or *iso*octane—although its straight octane number is lower, 81 versus 97 and 100, respectively.

The oxygen bomb stability of polymer gasoline is low, but its inhibitor susceptibility is high.

ACKNOWLEDGMENT

Grateful acknowledgment is hereby made for the assistance of B. B. Corson, E. R. Kanhofer, W. H. Hubner, and F. J. Skowronski.

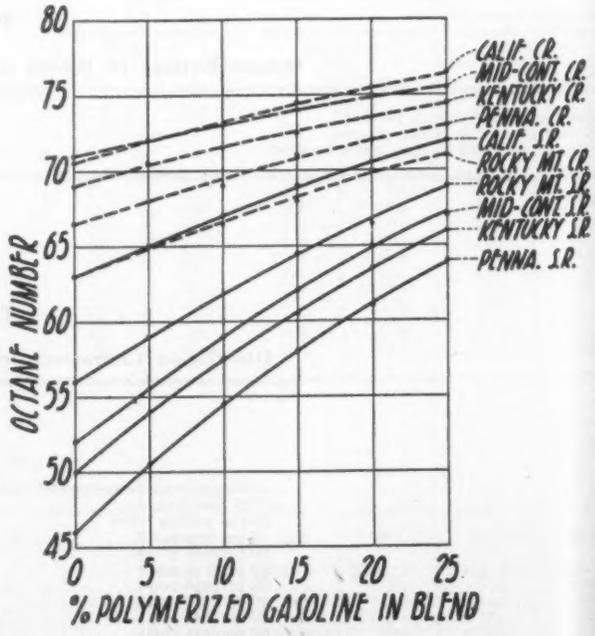

FIGURE 2

Blending Value of Polymerized Gasoline When Blended with Straight-run and Cracked Gasolines from Various Crude Sources.

Chemical Constitution of the Gasoline Fraction of Petroleum

A. P. I. RESEARCH PROJECT 6

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THE work of the American Petroleum Institute's Fundamental Research Project 6 on the naphtha fraction of the crude petroleum which has been under investigation has reached the stage where it is possible to analyze critically, and with profit, the results obtained to date. The project has determined the chemical constitution of the major part of that fraction of a Mid-Continent petroleum normally boiling below 180° C. There have been actually identified and isolated 35 hydrocarbons; six other hydrocarbons have been detected and are in process of separation; and some 20 others are suspected to be present in significant amounts, and are in order for future investigation.

The resolution of the naphtha fraction into its major hydrocarbon constituents has been a work in virgin fields, with no precedents to follow. But now that the course has been charted and marked, the entry into this new territory can be made with considerable directness of purpose and assurance of return. The means which enable one to reach the goal of separating petroleum are the physicochemical fractionating tools of distillation, crystallization, adsorption, extraction, and carefully-controlled chemical treatment, together with appropriate variations and combinations of these.

The future work of the project with regard to the naphtha fraction will be: 1, to complete the separation and identification of the as yet undetermined constituents; and 2, to outline a general systematic method for separating the naphtha fraction of any crude petroleum into its major hydrocarbon constituents.

The author is director of A. P. I. Research Project 6, and publication has been approved by the director of the National Bureau of Standards, United States Department of Commerce. The Author acknowledges indebtedness to M. R. Fenske, R. T. Leslie and J. D. White for aid in preparing this paper.

ABOUT 15 yeears ago the petroleum industry began to undergo a profound change, because petroleum was beginning to attain a greatly increased utility to man. Modern civilization was requiring petroleum products for new services and for more specilized older ones. For example, almost any gasoline could operate satisfactorily the automobile of 1920, and many fuels were then evaluated more in psychological and aesthetic ways than in terms of utility and performance. But today automobile gasoline must be made so that its properties will conform to the requirements of the high speed high compression motor; and aviation gasoline must possess very special qualities to give the needed maximum power, reliability, and safety. In order to fill these and other new economic needs, the industry began to treat the crude oil in special ways to produce products of higher quality and a greater variety of properties. It was obvious that the petroleum industry could make better progress in attaining this new objective if it learned something definite about the chemical constitution of its raw material.

In 1928 one of the authorities on petroleum wrote: "... the isolation of pure compounds from petroleum is a matter of extraordinary defficulty ... only relatively few pure compounds have been separated from it." At that time the existing knowledge of the chemical constitution of petroleum was extremely meager; and the little definite information available was limited to the low boiling fractions, with the knowledge of the lubricating oil fraction being based chiefly upon surmise and conjecture. This slow progress in determining the chemical constituents of petroleum was caused by the lack of interest and support, and by the failure to bring to bear upon the problem all the possible tools of physical chemistry.

But in 1927 circumstances had already conspired to bring both of these urgent needs to the aid of the particular problem of investigating in a systematic way the hydrocarbon constituents of petroleum. The industry, through the American Petroleum Institute, provided the necessary interest and financial support; and the National Bureau of Standards provided the laboratory space, certain supplies and apparatus, and the necessary direction of the project in the person of the late Edward W. Washburn, one of the outstanding physical chemists of the world.

The work of Research Project 6 and the methods and apparatus employed were summarized in 1933 by Washburn* in a report to the American Petroleum Institute at its annual meeting that year. It seems appropriate at this point to acknowledge the great debt which science and industry owe to E. W. Washburn for his enthusiastic leadership and guidance of the work of the project. The success of that work is in large measure due to the nonchalance with which the old-established conventions were disregarded and

*A complete list of the publications of Research Project 6 is given at the end of this paper. Literature references to any particular method or apparatus will be found in the appropriate paper in that list.

to the readiness with which every new physical method of separation was investigated.

SYSTEM OF FRACTIONATION

The system of separating petroleum into its constituents which has resulted from the work of this project may be described briefly as the systematic interlocking, combination, and variation of all the feasible methods of fractionation. The resolution of the naphtha fraction into its component hydrocarbons has involved working in virgin fields, with no precedents to follow. But now that the paths are in general rather well defined, the entry into this new territory can be made with considerable directness of purpose and assurance of profit. The means which enable one to reach this goal are the physico-chemical fractionating tools of distillation crystallization, adsorption, extraction, and carefully controlled chemical treatment, together with appropriate variations and combinations of these.

However, these methods of fractionation are not new to the petroleum industry, which has been using them in one form or another for many years: distillation has been the prime method of fractionating petroleum; crystallization has been used to remove paraffin-type hydrocarbons from lubricating stock in the dewaxing process; adsorption has been used in the refining of distillates and residuals by the use of clays, fuller's earth, etc.; and extraction has come into great prominence in the industry in the improvement of the quality of lubricating oils by treatment with solvents.

The contributions of Project 6 to the problem of fractionation may be said to be in the field of refinement, improvement, and variation of the different methods of separation, and the systematic interlocking of them to solve particular problems. For example, the variations in the different general methods of fractionation include:

1. *Distillation: a,* alteration of pressure (760 to 0.0001 mm. mercury); *b,* addition of another substance.

Alteration of the pressure permits fractionation of an azeotropic (minimum- or maximum-boiling) mixture because the conposition of the latter changes with pressure. Distillation at reduced pressure is also necessary in the case of those substances which tend to decompose at their normal boiling points.

Distillation in the presence of an appropriate added substance, such as alcohol or acetic acid, permits fractionation of a constant-boiling mixture; because the added substance forms an azeotropic (minimum- or maximum-boiling) mixture with one or more of the components.

2. *Crystallization: a,* simple refrigeration; *b,* refrigeration in an appropriate solvent.

Simple refrigeration is usually successful when the wanted component is present in the given fraction in large amount and when it has a not too low freezing point. Mixtures of large unsymmetrical molecules having a low freezing point usually become very viscous before the freezing point is reached, and in these cases simple refrigeration results in glassy solid mixtures.

Refrigeration with an appropriate solvent permits crystallization of the wanted component by increasing its mobility in the liquid state at the temperature of crystallization.

3. *Adsorption:* Variations in this method of fractionation are obtained by using different absorbent materials, which differ in selectivity and capacity.

4. *Extraction:* Variations in fractionating by extraction are obtained by using different solvents which have different selective solubilities for the various components of the mixture.

The simple process of fractional distillation has itself been remarkably improved in the past decade. Liquids which were formerly considered inseparable by distillation now are easily separated in efficient rectifying columns. This is important to the present problem; because, with few exceptions, the first fractionating tool to be used on any crude cut is that of efficient distillation, whereby the fraction is separated into a series of substantially constant-boiling fractions.

Distillation at pressures below atmospheric is, in certain cases, advantageous in separating two components. For example, there is evidence that the vapor-pressure—temperature curves of a paraffin and a naphthene normally boiling near the same temperature cross each other, so that in a certain pressure range the paraffin is more volatile than the naphthene, while in another pressure range the naphthene is the more volatile.

Examples of the utility of adding appropriate other substances in order to break up, by distillation, an otherwise constant boiling fraction are: **a,** the use of methyl or ethyl alcohol in separating the abnormal mixture of hexane and benzene, which cannot be completely separated by simple distillation; and, **b,** the use of glacial acetic acid in separating an ideal solution of a paraffin and a naphthene normally boiling near the same temperature. The latter method is useful for separating the appropriate hydrocarbons boiling in the range from about 100 to 180°C.

Crystallization by simple refrigeration is especially useful in separating some of the normal paraffins which have been previously concentrated into given cuts by distillation. The usual method here is that of equilibrium melting where the entire cut is first solidified and thoroughly mixed to secure homogeneity; and then, as the temperature is raised, most of the impurities are centrifuged off as a liquid from the more or less pure crystals of the wanted hydrocarbon. It is possible to obtain hydrocarbons of a very high degree of purity by this method.

When the given cut contains no one hydrocarbon in large amount, and when the freezing point is low, the fraction will usually solidify to a glass on cooling —and the method of crystallization from a solvent must be used. For this purpose it is necessary to select a suitable liquid solvent which itself does not freeze at the given temperature. Liquid methane, ethane, propane, the halogenated methanes, and methyl and ethyl either can be used advantageously as solvents which will permit crystallization of a hydrocarbon which cannot otherwise be crystallized because of its viscous nature at the freezing temperature.

In the method of fractionation by extraction an appropriate liquid solvent is selected in which the constituents of the given petroleum fraction will distribute themselves in proportions other than those which they have in the fraction itself. For example, aromatic hydrocarbons are more soluble in liquid sulfur dioxide than are the paraffins and naphthenes, and this method becomes extremely useful in removing the aromatic hydrocarbons from the other types.

The use of the method of adsorption in fractionating hydrocarbons is a more recent development in

the work of the project. By means of adsorption with silica gel, it has been found possible to remove effectively the aromatic constituents from a given fraction. Because the capacity of the gel in this regard is small, being about 1 g. of aromatic hydrocarbon per 10 g. of silica gel, this method has its greatest utility in completely stripping a given fraction of its aromatic constituents after the main bulk of the latter has been removed with sulfur dioxide. It is also possible to effect a small but significant separation of naphthenic from paraffinic hydrocarbons by means of adsorption with silica gel.

ANALYSIS OF THE CONSTITUTION OF THE NAPHTHA FRACTION

It is the main purpose of this paper to give a summary of all the information which Research Project 6 has obtained to date on the chemical constitution of the naphtha fraction of the Mid-Continent petroleum which has been under investigation. Leslie and White have just completed a critical study and analysis of all the data obtained by the entire project on the gasoline fraction of this petroleum, and the information contained in their report is displayed graphically in the accompanying figures and tables.

Figure 1 gives a graphical history of the 1000 gallons of selected Mid-Continent crude oil supplied to the project by Marland Oil Company from its well No. 6 in the South Ponca field, Kay County, Oklahoma. The assay distillation is recorded at the bottom of the figure. This oil was first distilled in a semi-commercial column by Sun Oil Company. Then, in the laboratory of the project at the National Bureau of Standards, the naphtha fraction was distilled in a 15-liter metal still provided with a 20-plate column, and subsequently in 30-plate all-glass rectifying stills. The naphtha fraction now was fractionated

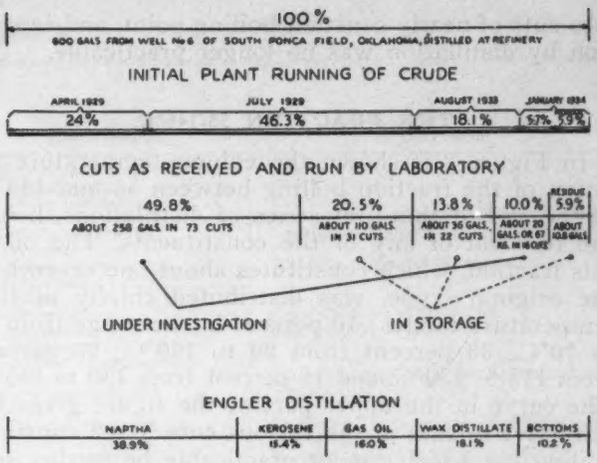

FIGURE 1

History and Status of Work on the Analysis of a Mid-Continent Petroleum

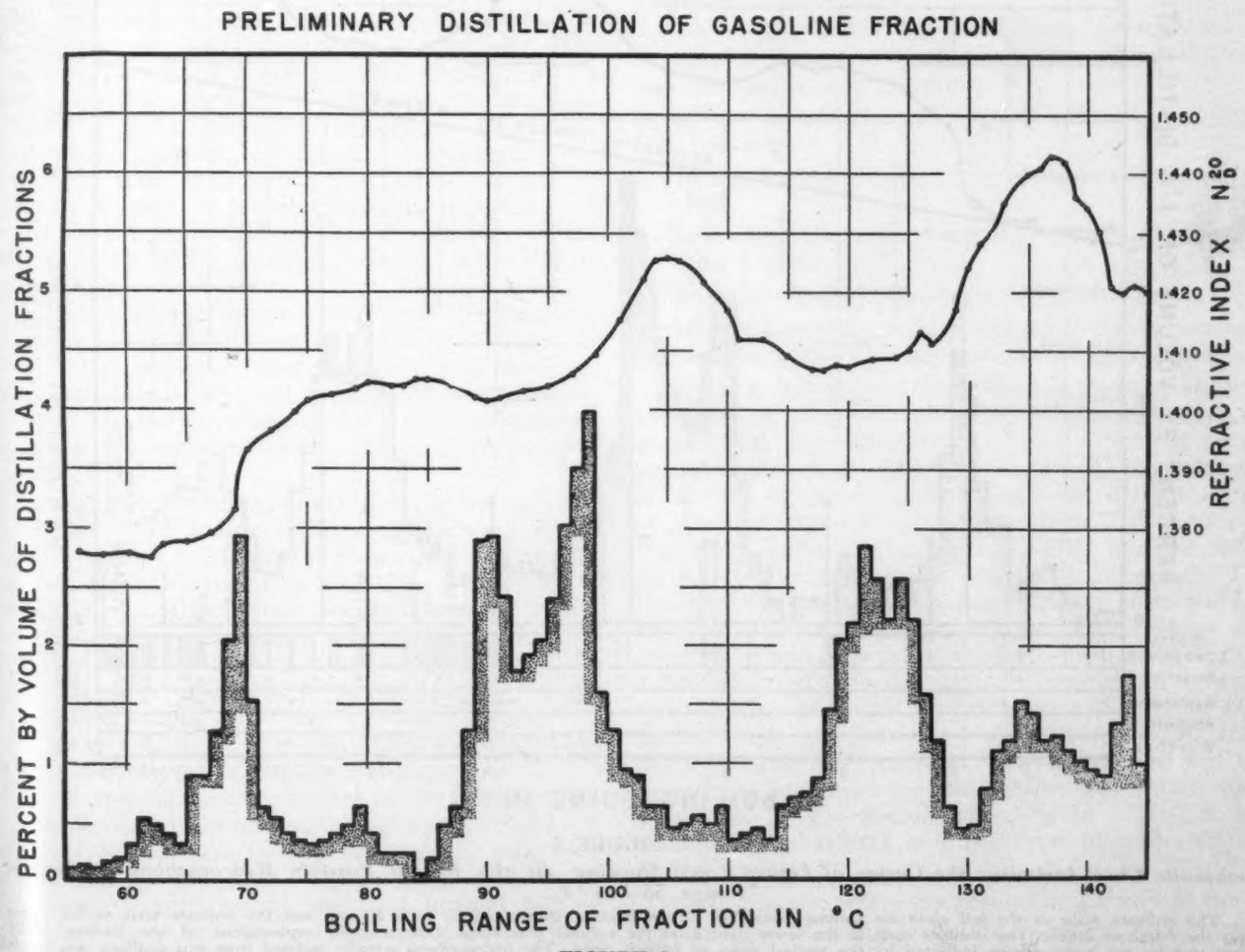

FIGURE 2

Volume -Temperature Distillation Curve of the Fraction 55-145°C. Before Removal of Any Constituents

The ordinate scale on the left gives the volume percentage of the fraction 55-145°C. constituted by each one-degree cut. The upper curve in the figure, with the ordinate scale on the right, gives the refractive index. The scale of abscissae gives the boiling temperature in °C. (at 760 mm.)

into cuts of nearly constant boiling point, and separation by distillation was no longer practicable.

THE FRACTION 55-145°C.

In Figure 2 is shown the volume-temperature relation of the fraction boiling between 55 and 145°C. at the end of this first series of distillations, before the removal of any of the constituents. The oil in this fraction, which constitutes about one seventh of the original crude, was distributed chiefly in four temperature ranges: 10 percent in the range from 65 to 70°C., 30 percent from 90 to 100°C., 25 percent from 115 to 130°C. and 15 percent from 130 to 145°C. The curve in the upper part of the figure gives the refractive indices of the various cuts. Each constant-boiling cut which cannot practicably be further separated by distillation may consist of:

a. a substantially pure substance;

b. an ideal solution of two or more hydrocarbons whose boiling points normally lie quite close together; or

c. an azeotropic (minimum- or maximum-boiling) mixture of two or more hydrocarbones.

In order to fractionate these practically constant-boiling cuts, a variation in the method of distillation, some form of crystallization, extraction, adsorption, or carefully-controlled chemical treatment, or any combination of these, was used. Thus, in case (*a*), which is rarely encountered in actual practice, the wanted constituent was separated from its impurities and in cases (*b*) and (*c*) one or more of the components were removed. Subsequent to this separation, straight distillation in highly efficient stills was again used, and a new set of constant-boiling fractions obtained. Then the interlocking process of separation proceeds.

In Figure 3 are shown the curves exhibited in Figure 2, together with information which portrays the complexity of the task of separating the con-

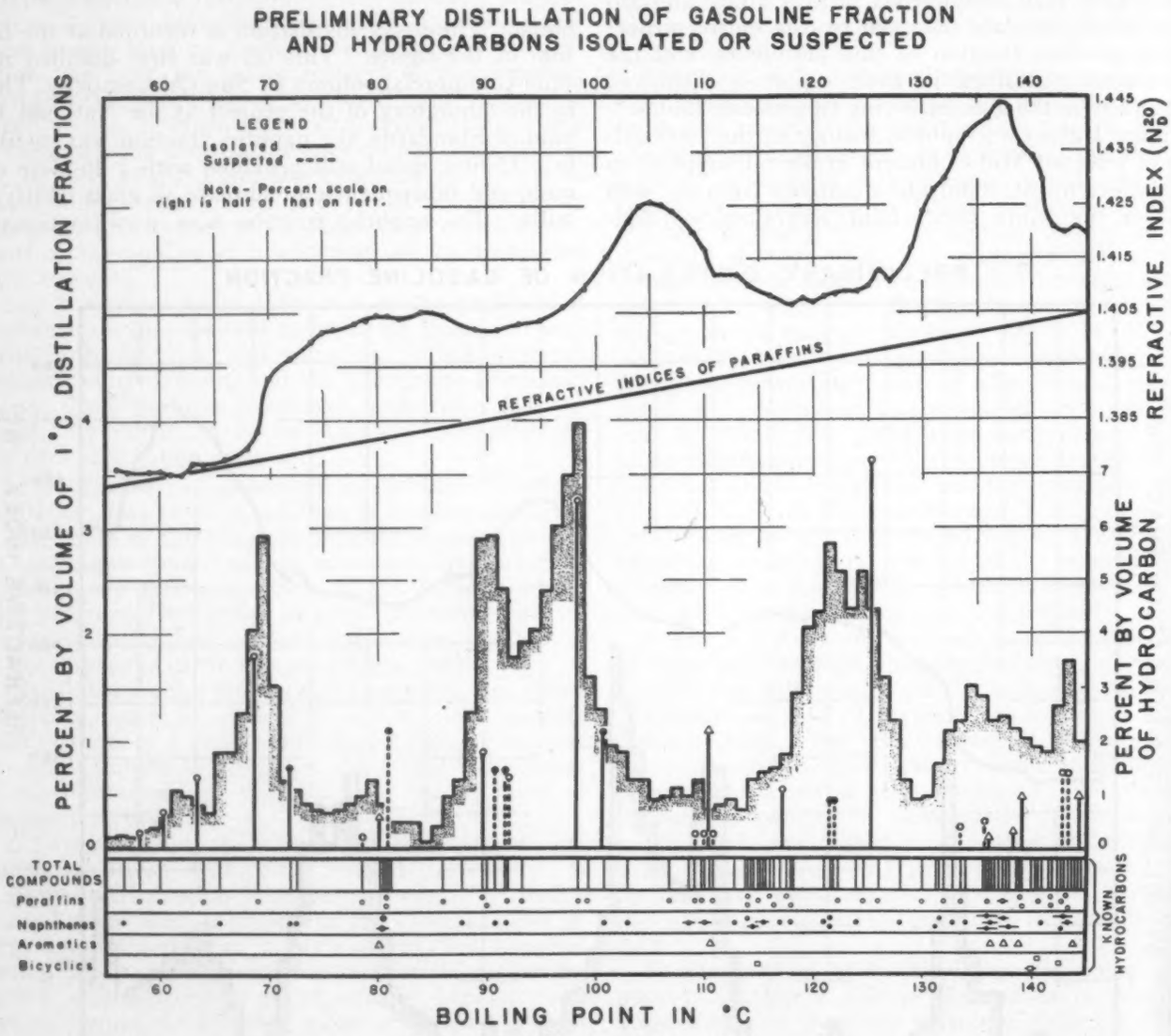

FIGURE 3

Composite Chart Including the Curves of Figure 2 and Showing All the Known Possible Hydrocarbons Boiling in the Range 55-145 ° C.

The ordinate scale on the left gives the volume percentage of the fraction constituted by each 1° cut, and the ordinate scale at the upper right gives the refractive index. The ordinate scale in the lower right gives the volume percentage (see text for explanation) of the fraction 55-145° C. constituted by the hydrocarbons indicated by the vertical solid or broken lines. The hydrocarbons actually isolated from this distillate are indicated by the solid vertical lines, and those detected by the dotted lines. The scale of abscissae gives the temperature in °C.

The horizontal section labeled "total compounds" indicates at the appropriate temperature all the known hydrocarbons that are reported to boil in the range from 55 to 145°C. The four lowermost horizontal sections indicate the types of the given hydrocarbons. A horizontal line through a symbol indicates the uncertainty in the boiling point.

The diagonal line below the refractive-index curve represents the average value of the refractive index for the paraffin hydrocarbons.

TABLE 1
Analysis of Figure 3

Constant-boiling Fraction		Types of Constituents	Names of Chief Constituents	Method of Separation or Detection[2]
Approximate Boiling Range (Deg. C.)	Class[1]			
58-65	*a*	Paraffinic	2,3-Dimethylbutane	Distillation.
(Resolved into three fractions by further distillation)			2-Methylpentane	Distillation.
			3-Methylpentane	Distillation.
65-71	*c*	Paraffinic	*n*-Hexane	Distillation with methyl and ethyl alcohol nitration followed by crystallization.
		Naphthenic	Methylcyclopentane	
		Aromatic	Benzene	
76-81	*b*	Paraffinic	2, 2-Dimethylpentane	Nitration followed by crystallization.
		Naphthenic	Cyclohexane	
		Aromatic	Benzene	
			2-Methylhexane	Crystallization with solvent.
85-92	*b*	Paraffinic	3-Methylhexane	Suspected from R. I. curve.
		Naphthenic	1, 2-Dimethylcyclopentane	
			1, 3-Dimethylcyclopentane	
95-101	*c*	Paraffinic	*n*-Heptane	Nitration followed by distillation and crystallization.
		Naphthenic	Methylcyclohexane	
		Aromatic	Toluene	
107-110	*b*	Paraffinic	2, 5-Dimethylhexane	Suspected from volume of distillate and R. I. curve.
		Aromatic	2, 4-Dimethylhexane	Toluene separated by nitration.
			2, 2, 3-Trimethylpentane	
			Toluene	
115-127	*b*	Paraffinic	*n*-Octane	Crystallization with and without solvent.
		Naphthenic	2-Methylheptane	
			m-Dimethylcyclohexane	
			p-Dimethylcyclohexane	
131-141	*c*	Paraffinic	2, 5-Dimethylheptane	Paraffins suspected from volume of distillate and R. I. curve.
		Aromatic	2, 4-Dimethylheptane	Aromatics isolated by extraction and sulfonation.
			o-, *m*-, and *p*-Xylenes	
			Ethylbenzene	
142-144	*b*	Paraffinic	2-Methyloctane	Paraffins suspected from R. I. curve.
		Aromatic	3-Methyloctane	
			o-Xylene	Aromatic isolated by extraction and sulfonation.

[1] (*a*) Indicates a substantially pure substance; (*b*) an ideal solution of two or more hydrocarbons having nearly identical boiling points; (*c*) an azeotropic (minimum- or maximum-boiling) mixture.
[2] R. I.=refractive index.

stituent hydrocarbons. In the horizontal section, immediately below the volume-temperature curve, are shown, by means of short vertical lines at the appropriate temperatures, the known possible hydrocarbons which may be constituents of the oil. The character of each of these possible constituents is indicated in the four next lower horizontal sections of Figure 3 to be paraffinic, naphthenic (saturated monocyclic), aromatic, or bicyclic (saturated). For each given type of hydrocarbon, both the boiling point and number of possible isomers increase with the size of the molecule, so that the number of the possible constituents increases greatly with rise in boiling point.

The diagonal line drawn just below the curve of refractive index represents the average values of the refractive indices of the paraffinic hydrocarbons. Horizontal lines at about 1.42 and 1.50 would represent approximately average values for the naphthenic (saturated monocyclic) and aromatic hydrocarbons, respectively.

The solid perpendicular lines drawn in the volume-temperature plot indicate the hydrocarbons which were sufficiently predominant in the first set of constant-boiling fractions to be isolated. The types of these isolated hydrocarbons are indicated by appropriate symbols. The height of each of these lines represents roughly the percentage of the fraction 55-145°C. which is estimated to be constituted by the given hydrocarbon. The dotted lines represent, in a similar way, some less abundant hydrocarbons whose presence was later made evident.

Table 1 summarizes the nature of the substantially constant-boiling fractions which appear in Figure 3. Three are of the class (*a*), or substantially pure substances; five of the class (*b*), or ideal solutions of components having nearly identical normal boiling points; and three of class (*c*), or azeotropic mixtures (minimum- or maximum-boiling). The last named are attributable to the presence of the aromatic hydrocarbons, benzene, toluene, and the xylenes. The presence of these aromatic hydrocarbons is indicated by the sharp rise in the refractive index at the appropriate temperature.

The hydrocarbons separated from the first set of constant-boiling fractions, by means of crystallization, extraction, etc., include:

1. All the possible normal paraffins: hexane, heptane, octane.
2. All the 2-methyl derivatives of these normal paraffins.
3. Two other isomers of hexane: 2,3-dimethylbutane and 3-methylpentane.
4. Methylcylopentane and methylcylohexane.
5. All the possible aromatic hydrocarbons: benzene, tolune, ethylbenzene, and the three xylenes.

Figure 4 shows the volume-temperature relation of the fraction after the foregoing compounds were removed and the fraction was again subjected to repeated distillation. As was expected, the removal of the major constituents caused the disappearance of some of the volume peaks which are shown in Figure 3; other volume peaks have become more prominent; and some new ones have appeared. The changes in refractive index have become more marked because of the closer fractionation attainable by distillation of the now less complex mixture. In Figure 4 are indicated by solid vertical lines, in the volume-temperature plot, the hydrocarbons that were separated from this second set of constant-boiling fractions. Those hydrocarbons whose presence was detected are indicated by the broken lines, and those suspected by the dotted lines. As in Figure 3, the known hydrocarbons and the type of molecule are indicated.

Table 2 summarizes the results of a study of the 10 new constant-boiling fractions indicated in Figure 4. All the constituents present in significant amount in the region from 55 to 75°C. have been isolated and identified, and all the oil remaining in the region 98

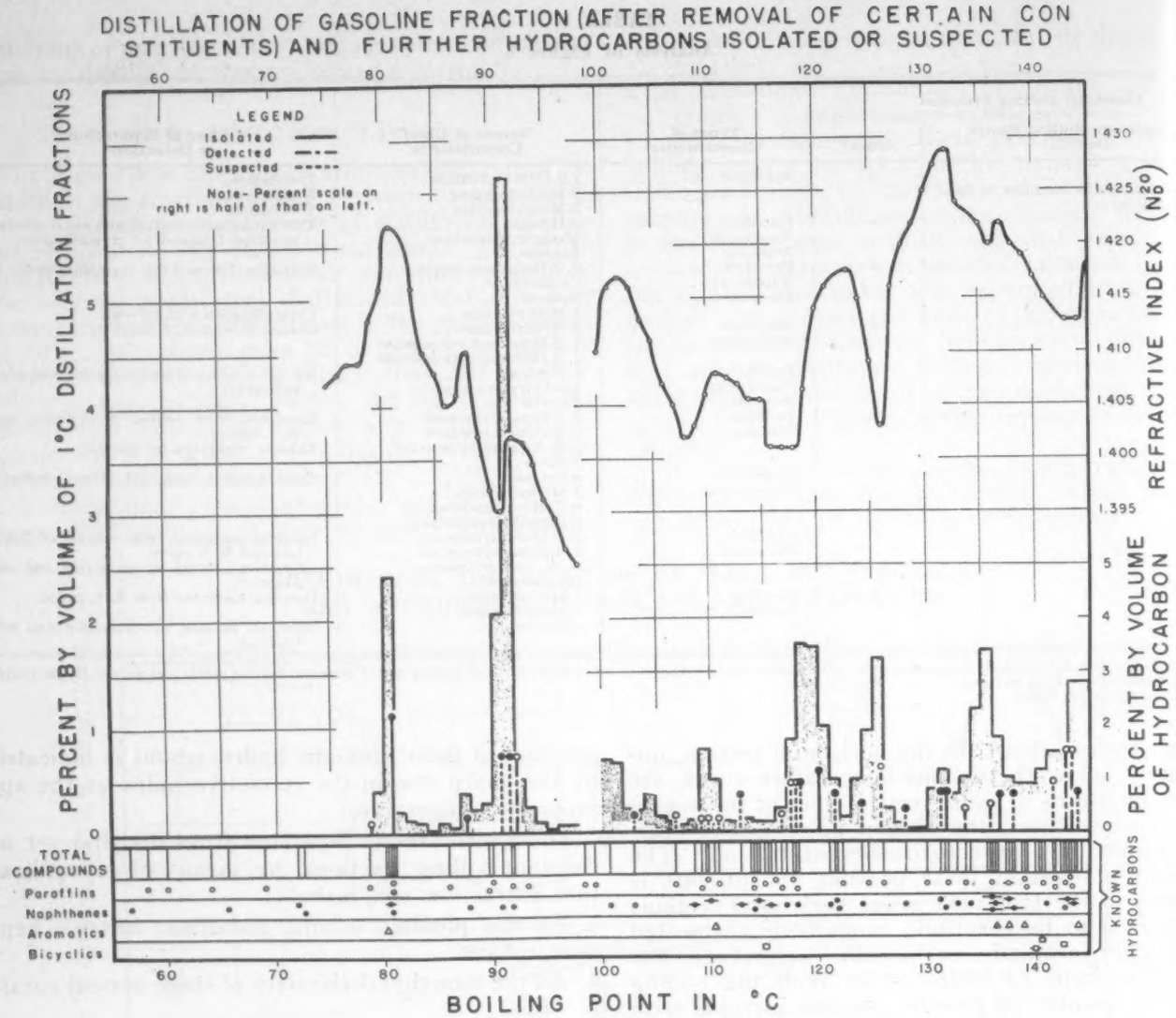

FIGURE 4

Composite Chart Giving the Volume-Temperature Distillation Curve After the Removal of Certain Constituents
(See legend of Figure 3 and text for explanation.)

TABLE 2
Analysis of Figure 4

Constant-boiling Fraction				
Approximate Boiling Range (Deg. C.)	Class[1]	Types of Constituents	Names of Chief Constituents	Method of Separation or Detection[2]
79- 81	*b*	Naphthenic...	Cyclohexane	Crystallization.
		Paraffinic....	2, 2-Dimethylpentane	
87- 89	*a*	Naphthenic...	1, 1-Dimethylcyclopentane	Crystallization.
90- 92	*b*	Naphthenic...	1, 2-Dimethylcyclopentane	Suspected from R. I. curve.
		Paraffinic....	1, 3-Dimethylcyclopentane	3-Methylhexane detected by R. I. and chlorosulfonic-acid treatment.
			3-Methylhexane	
103-106	*b*	Naphthenic...	Ethylcyclopentane	Suspected from volume of distillate and R. I. curve.
		Paraffinic....	2, 2, 3, 3-Tetramethylbutane	
109-111	*b*	Naphthenic...	1, 2, 4-Trimethylcyclopentane	Suspected from volume of distillate and R. I. curve.
		Paraffinic....	2, 5-Dimethylhexane	
			2, 4-Dimethylhexane	
			2, 2, 3-Trimethylpentane	
117-122	*b*	Paraffinic....	3, 4-Dimethylhexane	Crystallization with solvent or suspected from volume of distillate and R. I. curve.
		Naphthenic...	4-Methylheptane	
			3-Methylheptane	
			Cycloheptane	
			m-Dimethylcyclohexane	
			p-Dimethylcyclohexane	
123-127	*b*	Paraffinic....	(*n*-Octane)	Suspected from volume of distillate and R. I. curve.
		Naphthenic...	2, 2, 5-Trimethylhexane	
			1-Methyl-2-ethylcyclopentane	
			o-Dimethylcyclohexane	
130-132	*b*	Naphthenic...	Ethylcyclohexane	Crystallization with solvent. The cyclopentane suspected from R. I. and freezing point behavior.
			n-Propylcyclopentane	
134-137	*b*	Paraffinic....	2, 4-Dimethylheptane	Nonanaphthene isolated by crystallization. Others detected after subsequent fractionation.
		Naphthenic...	2, 5-Dimethylheptane	
			Nonanaphthene	
			1, 3, 5-Trimethylcyclohexane	
140-145	*b*	Paraffinic....	2-Methyloctane	Detected from volume of distillate, R. I. curve, and subsequent fractionation.
		Naphthenic...	3-Methyloctane	
			4-Methyloctane	
			1, 2, 4-Trimethylcyclohexane	

[1] (*a*) Indicates a substantially pure substance; (*b*) an ideal solution of two or more hydrocarbons having nearly identical boiling points; (*c*) an azeotropic (minimum- or maximum-boiling) mixture. [2] R.I.=refractive index.

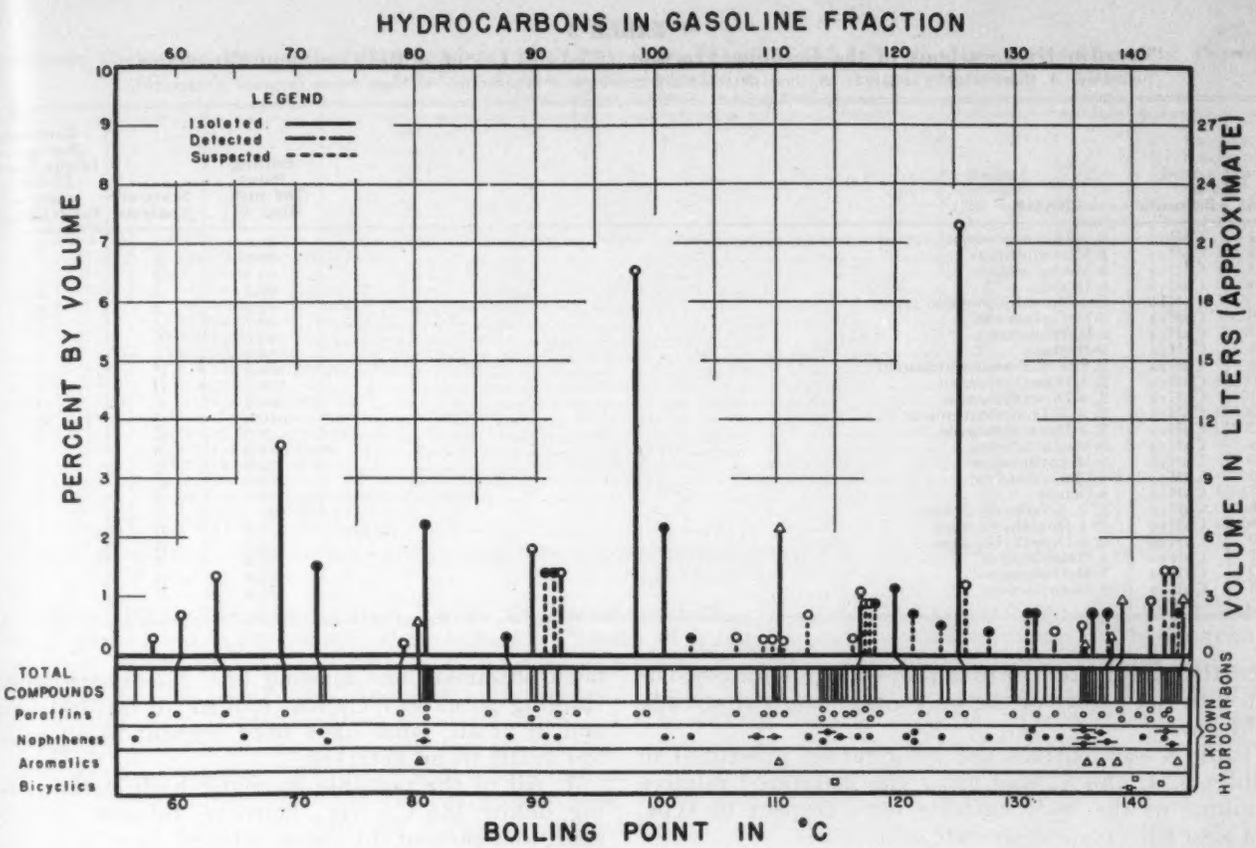

FIGURE 5

Composite Chart of the Hydrocarbons in the Gasoline Fraction 55-145 ° C., Including: ———, Those Hydrocarbons Actually Isolated and Identified; — — — —, Those Detected and in Process of Separation; - - - - - - -, Those Whose Presence in Significant Amount is Suspected.

The vertical lines above the zero abscissa indicate roughly (see text for explanation) the percentage of the fraction (scale to left) which is estimated to be constituted by the given hydrocarbon. The ordinate scale on the right gives the actual volume handled. The type of hydrocarbon is indicated by appropriate symbols, as explained in the lower sections. The known possible hydrocarbons are indicated, as before, in the horizontal section labeled "total compounds." The scale of abscissae gives the boiling temperature in deg. C. (at 760 mm.).

to 100°C. has been attributed to normal heptane and methylcyclohexane.

A study of Figure 4 indicates that, once the aromatic compounds have been removed, no pronounced tendency to form azeotropic mixtures exists. With the exception of the fraction 87-89°C., all the constant-boiling fractions appearing in Figure 4 can be explained as ideal solutions of two or more hydrocarbons having nearly identical normal boiling points. The one exception may also be explained by considering it to be of the ideal-solution type in which the minor components were present in amounts too small to be detected.

Figure 5 indicates the type and amount of each of the various hydrocarbons which have been actually isolated from the fraction 55-145°C., together with those hydrocarbons detected and in process of separation and those hydrocarbons whose presence in this fraction in significant amount is suspected. The solid lines indicate the hydrocarbons actually isolated; the broken lines, those detected and in process of separation; and the dotted lines, those whose presence is suspected. The ordinate in each case indicates roughly the estimated percentage of the fraction 55-145°C. which is constituted by the given hydrocarbon.

Figure 5 may be said to represent all the information which the project has obtained to date on the hydrocarbon constituents of the gasoline fraction (55-145°C.) of this petroleum.

In Tables 3, 4, and 5 are listed, according to boiling point, state of analysis, and (roughly) percentage content in the fraction 55-145°C., all the various paraffinic, naphthenic (saturated monocyclic), and aromatic hydrocarbons given in Figure 5. In these three tables are listed 47 different hydrocarbons, which number is to be compared with the total of 88 known hydrocarbons reported to boil in the range from 55 to 180°C.

It is to be emphasized that, because the determination of the percentage of a given hydrocarbon in the petroleum is subordinate to the main problem of separation and identification, and because unknown losses occurred all along the way of these pioneering experiments, the figures representing the percentage content must be considered to be rough approximations only. As will be seen from the more detailed report of Leslie and White, the values in the last column of Tables 3, 4, and 5, and the values in Figures 3, 4, and 5 for the individual hydrocarbons, are probably too low by about 50 to 75 percent; but are, nevertheless, fairly representative of the relative amounts. Since it was the original intention to obtain only the order of magnitude of the percentage content of the identified hydrocarbons, the fact that the estimated percentage contents for the hydrocarbons of the gasoline fraction may add up to only about 60 percent is gratifying rather than disturbing. When the entire naphtha fraction has been worked out, it will be possible to adjust the values of the percentage content more nearly to represent the actual amounts present. Meanwhile, the figures are

TABLE 3

Paraffin Hydrocarbons in the Gasoline Fraction (55-145° C.) of a Mid-Continent Petroleum

Including: *A*, those actually isolated; *B*, those detected and in process of separation; *C*, those whose presence is suspected.

No.	Formula	NAME	Boiling Point (760 mm.) (Deg. C.)	State of Analysis	Estimated Percentage in the Fraction 55-145° C. (see text, for explanation)
1	C_6H_{14}	2, 3-Dimethylbutane	58.0	*A*	0.30
2	C_6H_{14}	2-Methylpentane	60.4	*A*	0.65
3	C_6H_{14}	3-Methylpentane	63.3	*A*	1.30
4	C_6H_{14}	*n*-Hexane	68.7	*A*	3.60
5	C_7H_{16}	2, 2-Dimethylpentane	78.9	*A*	0.20
6	C_7H_{16}	2-Methylhexane	89.7	*A*	1.80
7	C_7H_{16}	3-Methylhexane	92.0	*B*	1.45
8	C_7H_{16}	*n*-Heptane	98.4	*A*	6.50
9	C_8H_{18}	2, 2, 3, 3-Tetramethylbutane	106.8	*C*	0.30
10	C_8H_{18}	2, 5-Dimethylhexane	109.2	*C*	0.25
11	C_8H_{18}	2, 4-Dimethylhexane	109.9	*C*	0.25
12	C_8H_{18}	2, 2, 3-Trimethylpentane	110.8	*C*	0.25
13	C_8H_{18}	3, 4-Dimethylhexane	116.5	*C*	0.35
14	C_8H_{18}	2-Methylheptane	117.2	*A*	1.10
15	C_8H_{18}	3-Methylheptane	117.6	*C*	0.90
16	C_8H_{18}	4-Methylheptane	118.0	*C*	0.90
17	C_8H_{18}	*n*-Octane	125.4	*A*	7.25
18	C_9H_{20}	2, 2, 5-Trimethylhexane	126	*C*	1.20
19	C_9H_{20}	2, 4-Dimethylheptane	133.5	*B*	0.40
20	C_9H_{20}	2, 5-Dimethylheptane	135.9	*B*	0.50
21	C_9H_{20}	4-Methyloctane	141.6	*B*	0.95
22	C_9H_{20}	2-Methyloctane	142.8	*B*	1.45
23	C_9H_{20}	3-Methyloctane	143.4	*B*	1.45

reported unadjusted so that they will remain consistent with the values of the percentage content already published.

Table 6 summarizes the information presented in Tables 3, 4, and 5; and gives the estimated relative amounts of the hydrocarbons with respect to type, and also with respect to state of anaylsis.

THE FRACTION 145-180°C.

In the range from 145 to 180°C., predominant peaks in the volume-temperature distillation curve occurred near 150, 160 and 170°C. Normal nonane was isolated from the region around 150°C.; normal decane, from that around 170°C.; mesitylene, from that around 160°C.; and pseudocumene and hemimellitene, from the fraction 168-175°C. after the normal decane had been removed.

The hydrocarbons actually isolated from the fraction 145-180°C., together with rough estimates of the amounts present, are listed in Table 7. Although there are 80 hydrocarbons reported to boil in this range, about one third of the fraction 145-180°C. is constituted by the five hydrocarbons listed in Table 7.

Some of the hydrocarbons which are probably present in the remaining oil of the fraction 145-180°C. include: propylbenzene, ethyltoluene, butylbenzene, methylpropylbenzene, isomers of decane, and certain naphthenes.

SUMMARY FOR ALL THE FRACTIONS BOILING BELOW 180°C.

Table 8 lists all the hydrocarbons that have been actually isolated from the Mid-Continent crude by Research Project 6.

In connection with the work of the project on that part of the petroleum normally boiling below 180°C., the following points may be mentioned:

1. All the fraction below 100°C., except the cut 91-92°C., has been completely worked out.

2. No olefinic hydrocarbons are present in the fraction below 180°C., as shown by the zero iodine number.

3. Samples of hydrocarbons representing over half of the fraction 55-180°C. have been isolated and identified.

4. Four of the five possible isomers of hexane have been obtained. The missing one, 2,2-dimethylbutane (boiling point 49.7°C) was looked for but not found; and, if at all, must have been present in an amount too small to be detected.

5. All of the possible aromatic hydrocarbons boiling below 145°C.; viz., benzene, toluene, ethlybenzene, and each of the three xylenes, have been found. The three trimethylbenzenes have also been isolated.

6. The normal paraffin hydrocarbons from hexane to decane, inclusive, together constitute about one fifth of the fraction 55-180°C.

7. After the normal paraffins, the next more abundant hydrocarbons of the fraction 55-180°C. include: 2-methlyhexane, methlycyclopentane, cyclohexane, methlycyclohexane, toluene, and pseudocumene.

8. With the exception of these molecules having five or less carbon atoms, and four others indicated in Table 8, all the hydrocarbons listed in Table 8 were obtained with a purity of about 95 percent or better, and in most cases with a purity of 99 percent or better. One hydrocarbon, normal decane, was obtained with a purity of better than 99.99 percent.

9. Of the hydrocarbons listed in Table 8, 18 have not previously been actually isolated from any petroleum—the evidence for their presence, where reported, having been in most instances based upon the products obtained by chemical treatment of certain petroleum fractions or upon volume peaks in the distillation curve.

POSSIBLE BENEFITS TO THE INDUSTRY

The immediate benefits which may arise to the industry from a definite knowledge of the chemical constitution of petroleum, and of practical methods for separating the major chemical constituents, may be summarized, in general, as follows:

1. This knowledge will aid in the better utilization of petroleum for its various present and potential uses. The way will be made clearer for the practical separation of the crude into cuts differing in type of molecule as well as in size (boiling point). Separation by boiling point alone yields cuts possessing a conglomerate mixture of the properties of the paraffinic, naphthenic, and aromatic hydrocarbons. The separation both by type and size yields products

TABLE 4

Naphthene (Saturated Monocyclic) Hydrocarbons in the Gasoline Fraction (55-145 °C.) of a Mid-Continent Petroleum

Including: *A*, those actually isolated;
C, those whose presence is suspected.

No.	Formula	NAME	Boiling Point (760 mm.) (Deg. C.)	State of Analysis	Estimated Percentage in the Fraction 55-145° C. (see text, for explanation)
1	C_6H_{12}	Methylcyclopentane	71.8	*A*	1.45
2	C_6H_{12}	Cyclohexane	80.8	*A*	2.20
3	C_7H_{14}	1, 1-Dimethylcyclopentane	87.5	*A*	0.30
4	C_7H_{14}	1, 3-Dimethylcyclopentane	90.7	*C*	1.45
5	C_7H_{14}	1, 2-Dimethylcyclopentane	91.8	*C*	1.45
6	C_7H_{14}	Methylcyclohexane	100.8	*A*	2.20
7	C_7H_{14}	Ethylcyclopentane	103.0	*C*	0.30
8	C_8H_{16}	1, 2, 4-Trimethylcyclopentane	112.5-113	*C*	0.70
9	C_7H_{14}	Cycloheptane	118.1	*C*	0.90
10	C_8H_{16}	*m*-Dimethylcyclohexane	120.0	*A*	1.10
11	C_8H_{16}	*p*-Dimethylcyclohexane	121.7	*C*	0.70
12	C_8H_{16}	1-Methyl-2-ethylcyclopentane	124.0	*C*	0.50
13	C_8H_{16}	*o*-Dimethylcyclohexane	128.0	*C*	0.40
14	C_8H_{16}	*n*-Propylcyclopentane	131.3	*C*	0.70
15	C_8H_{16}	Ethycyclohexane	131.9	*A*	0.70
16	C_9H_{18}	Nonanaphthene (cyclopentane derivative)	136.7	*A*	0.65
17	C_9H_{18}	1, 3, 5-Trimethylcyclohexane	137-139	*C*	0.70
18	C_9H_{18}	1, 2, 4-Trimethylcyclohexane	143-144	*C*	0.70

possessing desired properties to a higher degree of quality and of a greater variety than before. These petroleum products with specialized properties can better satisfy the many new and specialized needs that the industry is being called upon to serve. A possible application of the foregoing lies in subjecting the gasoline fraction to a process of fractionation whereby those molecules that are excellent antidetonants (the aromatics and the highly branched paraffins) will be separated from those that are poor in this regard. In this way it might be possible to prepare in a practical way some of the gasoline of very high octane number that is needed for certain aviation uses.

2. The various chemical reactions, such as cracking, polymerization, etc., to which certain fractions of petroleum are subjected for the purpose of obtaining products with desired new properties, can be more profitably controlled. Given certain thermal data on heats of reaction and heat capacities, it is possible to determine, without the performance of a single equilibrium measurement, the optimum conditions of temperature and pressure for carrying out a given chemical reaction involving the disappearance of certain known molecules and the formation of certain other known molecules. In the cracking reaction, for example, the desired end products are known, but there is little information about what molecules are actually going into the cracking plant. Without a definite knowledge of the constitution of the charging stock, the full power of the methods of chemical thermodynamics cannot be utilized to control these reactions most economically—and recourse must be had to more or less empirical methods of control, sometimes at great cost to the industry. It is to be expected that for the reactions of cracking, polymerization, oxidation, hydrogenation etc., the more homogeneous the charging stock with respect to type and size of molecule, the easier it is to determine and maintain the optimum operating conditions, the more homogeneous is the nature of the products formed, and the greater is the yield of substances with the desired properties. It may be said, in general, that any refining process or reaction can be made to give better and greater yields, or to operate more economically, if there is available definite knowledge of the chemical constitution of the charging stock and of methods for making the charge more homogeneous with respect to both size and type of molecule.

3. The naphtha fraction of petroleum can become an important source of chemical compounds for use in industry and science. The use of petroleum as the source of some chemicals is already a matter of history. As the knowledge of the chemical constitution of petroleum increases, the industry can convert the laboratory methods of separation to a commercial basis, and obtain from the naphtha fraction many new chemicals which have or will find an important economic value. One can visualize the use of some of the hydrocarbon constituents as the starting point in the synthetic production of whole series of new substances useful to man. Developments along this latter line have been hampered both by a lack of chemical homogeneity in the oils used as starting materials and by a lack of knowledge of the methods for separating the mixture of products obtained. In this connection, it may be pointed out that the aromatic hydrocarbons (benzene, toluene, and the xylenes) present in one year's production of straight-

TABLE 5

Aromatic Hydrocarbons in the Gasoline Fraction (55-145° C.) of a Mid-Continent Petroleum

Including only: *A*, those actually isolated.

No.	Formula	NAME	Boiling Point (760 mm.) (Deg. C.)	State of Analysis	Estimated Percentage in the Fraction 55-145° C. (see text, for explanation)
1	C_6H_6	Benzene	80.2	*A*	0.60
2	C_7H_8	Toluene	110.5	*A*	2.20
3	C_8H_{10}	Ethylbenzene	136.1	*A*	0.20
4	C_8H_{10}	*p*-Xylene	138.4	*A*	0.30
5	C_8H_{10}	*m*-Xylene	139.2	*A*	0.95
6	C_8H_{10}	*o*-Xylene	144.4	*A*	0.95

TABLE 6

Summary of the Isolated, Detected, and Suspected Hydrocarbons in the 55-145° C. Fraction of a Mid-Continent Petroleum

TYPE	Isolated		Detected or Suspected		Total		Known Hydrocarbons Reported Boiling in the Range 55-145 Deg. C.
	No.	Estimated Relative Percentage	No.	Estimated Relative Percentage	No.	Estimated Relative Percentage	
Paraffins	9	40	14	20	23	60	41
Naphthenes[1]	7	15	11	15	18	30	37
Aromatics	6	10	..	..	6	10	6
Bicyclo-paraffins[2]	..	..	..	..	..	..	4
Total	22	65	25	35	47	100	88

[1]Saturated monocyclic.
[2]Saturated bicyclic.

TABLE 7

Hydrocarbons Isolated from the 145-180° C. Fraction of a Mid-Continent Petroleum

No.	Formula	Name	Boiling Point (760 mm.) (Deg. C.)	Estimated Percentage of the Fraction 145-180° C. (see text for Explanation)
1	C_9H_{20}	*n*-Nonane	150.72	15.5
2	$C_{10}H_{22}$	*n*-Decane	174.02	12.5
3	C_9H_{12}	Mesitylene (1, 3, 5-trimethylbenzene)	164.64	0.3
4	C_9H_{12}	Pseudocumene (1, 2, 4-trimethylbenzene)	169.2	3.
5	C_9H_{12}	Hemimellitene (1, 2, 3-trimethylbenzene)	176.1	0.9
Total				31.

TABLE 8

Hydrocarbons Isolated

No.	Formula	Hydrocarbon	Estimated Percentage in Crude (see text for explanation)	Purity of Best Sample (Mole Percent)	Published in RP No.[1]
		PARAFFINIC			
1	CH_4	Methane	[2]	[2]	...
2	C_2H_6	Ethane	[2]	[2]	...
3	C_3H_8	Propane	[2]	[2]	...
4	C_4H_{10}	*n*-Butane	[2]	[2]	...
5	C_5H_{12}	*n*-Pentane	[2]	[2]	...
6	C_5H_{12}	2-Methylbutane	[2]	[2]	...
7	C_6H_{14}	*n*-Hexane	0.5	98.3	239,311
8	C_6H_{14}	2, 3-Dimethylbutane	0.3	> 95	239,311
9	C_6H_{14}	2-Methylpentane			
10	C_6H_{14}	3-Methylpentane			
11	C_7H_{16}	*n*-Heptane	0.9	> 99.9	432
12	C_7H_{16}	2, 2-Dimethylpentane	0.03	54	458
13	C_7H_{16}	2-Methylhexane	0.25	99.9	542
14	C_7H_{16}	3-Methylhexane	[3]	[3]	...
15	C_8H_{18}	*n*-Octane	1.0	99.1	282
16	C_8H_{18}	2-Methylheptane	0.15	97	552
17	C_9H_{20}	*n*-Nonane	1.0	99.9	383
18	C_9H_{20}	2-Methyloctane	[3]	[3]	..
19	C_9H_{20}	2, 5-Dimethylheptane	[3]	[3]	...
20	$C_{10}H_{22}$	*n*-Decane	0.8	> 99.99	438
		NAPHTHENIC			
21	C_5H_{10}	Cyclopentane	[2]	[2]	...
22	C_6H_{12}	Methylcyclopentane	0.2	98.9	375
23	C_6H_{12}	Cyclohexane	0.3	99.98	360
24	C_7H_{14}	Methylcyclohexane	0.3	> 99.9	432
25	C_7H_{14}	1, 1-Dimethylcyclopentane	0.04	95	542
26	C_8H_{16}	1, 3-Dimethylcyclohexane	0.15	98	...
27	C_8H_{16}	Ethylcyclohexane	0.1	95	...
28	C_9H_{18}	Nonanaphthene	0.1	> 99	745
		AROMATIC			
29	C_6H_6	Benzene	0.08	99.8	311
30	C_7H_8	Toulene	0.3	[2]	280
31	C_8H_{10}	*p*-Xylene	0.04	> 99.9	501
32	C_8H_{10}	*o*-Xylene	0.12	> 99	501
33	C_8H_{10}	*m*-Xylene	0.12	> 99.9	501
34	C_8H_{10}	Ethylbenzene	0.03	94	554
35	C_9H_{12}	Hemimellitene	0.06	99.95	614
36	C_9H_{12}	Pseudocumene	0.2	99.9	614
37	C_9H_{12}	Mesitylene	0.02	99.95	614

[1]RP No. = Research Paper No. These papers are sold at nominal prices by the Superintendent of Documents, Government Printing Office, Washington, D.C
[2]Not determined.
[3]Determination in progress.

run gasoline alone are estimated to amount to about seven times that produced annually in the by-product coke industry.

It might be extremely profitable for the industry if fairly pure samples of the major constituents of petroleum were made available at reasonable cost to university and other scientific research laboratories. At present, for example, one kilogram of normal decane having a boiling range of about 2°C. costs about $150. This is prohibitive to the average research institution. Making these hydrocarbons readily available to investigators will result in the accumulation of important data on their properties and behavior, and will lead to the development of new economic uses for these substances.

CONCLUSION

The successful separation of the naphtha fraction of one petroleum into its major chemical constituents may now be said to be a reality in the laboratory. Although Research Project 6 has invested about 40 man-years of research in the determination of the chemical constitution of the major part of the 55-180°C. fraction of one petroleum, all of that work has been an adventure in unexplored territory. One could now, having charted and marked the course, accomplish the same results on any crude petroleum with a fraction of that effort.

The future work of the project with regard to the naphtha fraction will be: 1, to complete the separation and identification of the as yet undetermined constituents in that fraction of this Mid-Continent crude; and, 2, to outline a general systematic method for separating the naphtha fraction of any crude petroleum into its major chemical constituents.

PUBLICATIONS OF AMERICAN PETROLEUM INSTITUTE RESEARCH PROJECT 6

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Fundemental Research on the Chemical Constitution of Lubricating Oil . . .

A. P. I. RESEARCH PROJECT 6

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SOME of the available knowledge concerning the chemical constitution of petroleum is briefly reviewed. No definite, pure, individual hydrocarbon has ever been isolated from the lubricating-oil fraction of petroleum. The most effective means of separating the lubricating oil consists in the proper interlocking, combination, and variation of the physico-chemical fractionating methods of distillation, crystallization, extraction, and adsorption.

The work of Institute Research Project 6 on lubricating oil, now in progress about 1½ years, is reviewed. The lubricating oil fraction of a Mid-Continent crude oil was dewaxed, extracted with sulfur dioxide, and treated with silica gel in order to obtain a stable "water-white" portion, which has been subjected to four stages of systematic distillation. When this oil has been thoroughly fractionated with respect to size of molecules, fractionations with respect to type will be made, with the aim of obtaining closely-fractionated cuts containing hydrocarbons of like size and type. When this stage of separation is reached, the way will be made clear for the ultimate separation of pure hydrocarbons.

Presented at Mid-Year Meeting, American Petroleum Institute, Tulsa, May 15, 1935. Publication approved by the Director of the National Bureau of Standards, U. S. Department of Commerce.

The author is indebted to M. R. Fenske and B. J. Mair for aid in preparing this paper.

THE petroleum industry is closely allied with the business of automotive power and transportation; since petroleum furnishes not only the fuel for operating the engine, but also the oil for lubrication. Because of this dual utility of petroleum, the petroleum industry has had a double interest in the developments which have led to that product of modern technology, the present-day automobile. In addition to providing a fuel that will satisfactorily operate this machine, the industry must prepare an oil that will maintain a lubricating film between the extremely close fitting and very fast moving parts of this high powered engine.

The properties that characterize a good lubricating oil have been summarized many times, and include: oiliness or lubricity, resistance to decomposition and oxidation, small change of viscosity with temperature, and ability to flow freely in cold weather. In the past decade or so the industry has learned to treat the lubricating oil stock in various ways to enhance the value of the product with respect to any or all of the foregoing properties, as well as others; and the progress which has been made along these lines has been extraordinary when one considers that the refiner is dealing with a material whose actual chemical constitution is not known. The very fact of this progress, in the face of a lack of knowledge of the chemical constituents of the oil, presages the possible advances which the industry may make when something definite is learned about the chemical constitution of lubricating oil.

The extent of our present actual knowledge of what is lubricating oil may be summed up in the statement that from it not one pure, definite chemical compound has ever been isolated.

This does not mean, however, that nothing at all is known about lubricating oil. On the contrary, there has been amassed from various sources in the past 30 years a great many empirical data on the properties and behavior of lubricating oils. But all this information has been obtained on the more or less complex mixtures of hydrocarbons of various types and sizes (or molecular weights) which have constituted the samples upon which the measurements were made. These data pertain to an aggregation of a variety of hydrocarbon molecules; and, while careful analysis and interpretation of such data can yield some knowledge of the possible chemical constituents, no information is obtained as to the actual individual molecules present. Which is to say that the properties exhibited by a given mixture of three or more different hydrocarbons may be possessed by other mixtures containing some or all of the same hydrocarbons, but in other proportions. And the problem of making better lubricating oils for varied types of service should be simplified materially when there is available a knowledge of practical methods for better separating the mixture of hydrocarbons with respect to size and type of molecule.

Judging from what is known about the actual constituents of the gasoline fraction of petroleum [1a,2] the hydrocarbon molecules which are in the lubricating oil fraction may be expected to be made up of the following groups, separately or in combination: paraffinic groups, straight or branched chains; naphthenic groups, saturated rings (cyclopentane or cyclahexane nuclei, for example); and aromatic groups (benzene, naphthalene, etc., nuclei). And furthermore, the most likely combinations of these groups appear to be paraffinic-naphthenic

[a] Figures refer to bibliography at end of paper.

and paraffinic-aromatic—although there is no reason to suppose that in large hydrocarbon molecules, as in the lubricating oil fraction, a paraffinic group could not have attached to it both a naphthenic and an aromatic group. The hydrocarbon molecules in the lubricating oil fraction are likely to be mostly of the following types:

1. *Paraffinic:* Straight- or branched-chain saturated molecules having no ring structures. General formula, C_nH_{2n+2}.

2. *Naphthenic:* Molecules having one or more single, double, triple, etc., naphthenic-ring nuclei, with or without paraffinic side chains. General formula, $C_nH_{2n+2-2a}$, where a is the number of closed rings.

3. *Aromatic:* Molecules having one or more benzene, naphthalene, anthracene, etc., nuclei, with or without paraffinic side chains. General formula, C_nH_{2n-6b}, where b is the number of closed rings.

PRESENT KNOWLEDGE OF THE CHEMICAL CONSTITUTION OF LUBRICATING OIL

The early investigators who attempted to solve the very complex problem of the nature of the chemical constituents of the heavy fractions of petroleum were handicapped not only by the lack of modern apparatus and methods for chemical and physical analysis, but also by a lack of proper combination of the processes of fractionation. Their investigations consisted principally in determining the physical and chemical characteristics of more or less closely fractionated cuts of the lubricating oil stock. Because it appeared futile to attempt the separation of the oil into its actual chemical constituents, most of this work was concerned with the problem of obtaining, for these prepared fractions of lubricating oil, correlations between the physical and chemical properties on the one hand and the average chemical constitution on the other.

It seems appropriate to summarize here briefly the nature and extent of some of the available information on the chemical constitution of lubricating oil.[3, 4, 5]

Pioneer studies on the elementary composition of the lubricating oil fraction of petroleum were made by Mabery,[6] who found that the high-boiling fractions of Pennsylvania, Canada, and California oils had empirical formulas ranging from C_nH_{2n} to about C_nH_{2n-8}, the proportion of hydrogen decreasing with rise in boiling point. More recently, Mabery[7] attempted the fractionation, by extraction with hot mixtures of ether and alcohol, of the hydrocarbons in various crude oil residua not volatile at 300 °C. and a pressure of 30 mm. mercury. In this work Mabery obtained some fractions very low in hydrogen, having empirical formulas of about C_nH_{2n-20}. He reported molecular weights as high as 1700.

An extensive study of the lubricant fractions of a West Virginia petroleum was made by Smith,[8] who subjected the topped, dewaxed, and steam-distilled crude oil to successive extractions with acetone, and determined the physical properties of the fractions obtained. Smith found that the hydrocarbons poorer in hydrogen were more soluble, as were the hydrocarbons of lower molecular weight. The molecular weights varied from about 300 to 900, and the empirical formulas from C_nH_{2n-2} to C_nH_{2n-8}. From many data Smith concluded that a "study of the fractions . . . . does not disclose more than a suggestion as to the identity of the compounds of which these oils are composed," and that "consistency in the values of certain physical properties should assuredly not be construed as indicating that individual compounds have been separated." The work of this investigator emphasizes the complexity of the task confronting those who would separate the lubricating oil fraction into its constituent hydrocarbons.

Kyropoulos[9] correlated the data on refractive indices with the molecular weights of hydrocarbons of different types: normal and *iso*paraffins, naphthenes, and aromatic hydrocarbons. A separate curve of refractive index against molecular weight was obtained for each type, so that a determination of these two properties for any given fraction of lubricating oil permitted classification of it with respect to average constitution. Examination of the data for certain Pennsylvania and other saturated hydrocarbon oils led this investigator to believe that these oils are composed largely of *iso*paraffins.

In order to have a method for easily classifying oils with respect to type, ranging from Pennsylvania oils on the one hand to Gulf Coast oils on the other, Hill and Coates[10] investigated the relation between the viscosity and density of various oils. They were able to compute, from the values for viscosity and specific gravity of a given oil, a quantity called the "viscosity-gravity constant," whose value did not vary appreciably for oils of the same type, but did vary considerably for oils of different types. The value of the viscosity-gravity constant varies from about 0.80 for oils of the Pennsylvania type to about 0.90 for oils of the Gulf Coast type, and is extremely useful in spotting fractionation with respect to type of components.

In a somewhat similar endeavor, Dean and Davis[11] correlated the properties of viscosity and change of viscosity with temperature for various oils. They computed a quantity, called the "viscosity index," whose value was almost the same for oils of the same type (or for fractions of the same oil separated only by distillation) but varied considerably for oils of different types. The value of the viscosity index was set at about 100 for oils of the Pennsylvania type, and about 0 for unprocessed oils of the Gulf Coast type.

Utilizing the available data on the densities of pure hydrocarbons (of lower molecular weight than those to be expected in the lubricating oil fraction of petroleum) Davis and McAllister[12] obtained smooth relationships between molecular volume and molecular weight for each type or series of hydrocarbons, and between molecular volumes and the number of naphthene rings in the molecule. They deduced an equation which permitted calculation, for any aromatic-free oil, of the percentage of the total number of the carbon atoms that are in naphthene rings—given the molecular weight and specific gravity—and checked this on various fractions of lubricating oil by determination also of the average molecular formula. These investigators found, as has Fenske,[13] that the viscosity index of aromatic-free oils decreases, in general, with decrease in the value of x in the average molecular formula C_nH_{2n+x}.

McCluer and Fenske[14] desired to obtain an index involving viscosity and specific gravity, which would yield values numerically equal to the viscosity index. Accordingly, they devised the "gravity index," obtained from the relation between the viscosity-gravity constant and the viscosity index, and showed that for various mineral lubricating oils their gravity indices had values practically equal to the viscosity indices. But they found also that this identity between gravity index and viscosity index no longer existed in the case of synthetic lubricating oils made by polymerization of olefin hydrocarbons. This circumstance points to some constitu-

TABLE 1

Properties of Some Synthetic High-Molecular-Weight Hydrocarbons

(Values of kinematic viscosity interpolated from original data, using Cragoe's equation)

Reference	Name	Structure	Type	Formula	Value of x in the Formula C_nH_{2n+x}	Ratio $\frac{\text{No. H atoms}}{\text{No. C atoms}}$	Refractive Index n_D^{25}	Density d_4^{20}	Kinematic Viscosity		Saybolt Universal Viscosity		Viscosity Index	Viscosity-Gravity Constant	Gravity Index
									100 Deg. F. (Stokes)	210 Deg. F. (Stokes)	100 Deg. F. (Seconds)	210 Deg. F. (Seconds)			
16	16-*n*Butylhentriacontane	$CH_3-(CH_2)_{14}-CH(-(CH_2)_3-CH_3)-(CH_2)_{14}-CH_3$	Paraffinic	$C_{35}H_{72}$	2	2.06	1.4579	0.8237	0.2522	0.0541	122.5	44.1	151	0.767	....
17	1, 1-Dicyclohexylhexadecane	$(C_6H_{11})_2CH-(CH_2)_{14}-CH_3$	Naphthenic	$C_{28}H_{54}$	— 2	1.93	1.4832	0.8791	0.3292	0.0518	157.2	43.4	98	0.831	92
17	1-Cyclohexyl-2-hexahydrobenzylheptadecane	$C_6H_{11}-CH_2-CH(-CH_2-C_6H_{11})-(CH_2)_{14}-CH_3$	Naphthenic	$C_{30}H_{58}$	— 2	1.93	1.4871	0.8860	0.3052	0.0502	146.2	42.9	103	0.841	83
17	1, 1-Diphenylhexadecane	$(C_6H_5)_2CH-(CH_2)_{14}-CH_3$	Aromatic	$C_{28}H_{42}$	—14	1.50	1.5121	0.9135	0.2286	0.0423	112.0	40.4	108	0.879	28
17	1-Phenyl-2-benzylheptadecane	$C_6H_5-CH_2-CH(-CH_2-C_6H_5)-(CH_2)_{14}-CH_3$	Aromatic	$C_{30}H_{46}$	—14	1.53	1.5123	0.9165	0.3445	0.0512	164.3	43.2	85	0.877	31
18	Dihydro di-*B*-octylanthracene	$C_{14}H_{10}(-(CH_2)_7-CH_3)_2$	Aromatic	$C_{30}H_{44}$	—16	1.47	.....	0.948	2.93	0.1373	1,390	73.4	—9	0.894	—20
18	Dihydro di-*isoamyl*-anthracene	$C_{14}H_{10}(-(CH_2)_2-CH(-CH_3)_2)_2$	Aromatic	$C_{24}H_{32}$	—16	1.33	1.5640	0.972	5.40	0.1334	2,580	71.9	—210	0.922	....
18	1, 4-Di-*iso*-butylnaphthalene	$C_{10}H_6(-CH_2-CH(-CH_3)_2)_2$	Aromatic	$C_{18}H_{24}$	—12	1.33	1.5380	0.933	0.1408	0.0231	74.5	34.4	—284	0.910	....
18	Dihydrodiethylanthracene	$C_{14}H_{10}(-CH_2-CH_3)_2$	Aromatic	$C_{18}H_{20}$	—16	1.11	.....	1.014	0.3565	0.0323	169.8	37.2	—390	1.000	....

tional difference between these synthetic oils and the natural ones.

In a similar manner, other indices, such as the "boiling-point index" and the "optical index," have been devised in order to correlate the properties of oils with respect to their constitutional types.[15]

When a crude oil is fractionated with respect to size of molecules, as by distillation, the values of the various indices of viscosity, gravity, etc., are practically the same for all fractions; but, when the fractionation is made with respect to type, appreciable differences in the values of the indices will appear. One of the important uses of such indices, or other similar correlations, then lies in their indication, especially in combination with one another, of a fractionation by type of molecule.

PURE HYDROCARBONS OF HIGH MOLECULAR WEIGHT

There have appeared in the literature in the past several years accounts of the synthesis and properties of some hydrocarbons of the sizes and types that may be expected to be in the lubricating oil fraction of petroleum.[16, 17, 18] Table 1 lists a number of these hydrocarbons with their properties.* It is extremely interesting to note how the temperature coefficient of viscosity and the density, calculated in the form of the viscosity index and the viscosity-gravity constant or the gravity index, change with the structure of the molecule. One of the striking conclusions is that these relations are qualitatively in good agreement with the pre-conceived ideas developed from the study of lubricating oil fractions.

For the hydrocarbons in Table 1 the viscosity index is highest for the *iso*paraffin, being about 150; decreases to about 100 as two cyclohexyl groups are made part of the molecule, producing a two-ring naphthene; remains almost unchanged as these saturated rings are dehydrogenated to form two phenyl groups, producing a two-ring aromatic hydrocarbon; and then decreases very sharply to low values with increasing condensation of the molecule in the form of aromatic rings joined through two carbons atoms, as in the naphthalene and anthracene nuclei. For those hydrocarbons, with about the same number of carbon atoms in the molecule, there seems to be, in general, an increase in the values of both density and refractive index as the value of the viscosity index decreases. There is qualitative agreement between these data and the relation found by Davis and McAllister,[12] and confirmed by Fenske,[13] that the viscosity index of aromatic-free oils decreases, in general, with decrease in the value of x in the molecular formula C_nH_{2n+x}. A somewhat unexpected circumstance shown by Table 1 is the relatively small change in viscosity index produced by replacing, in a given molecule, two single naphthene rings by two single aromatic rings (compare the second and fourth and the third and fifth compounds.)

It would seem very desirable for the petroleum industry to encourage investigators in university and other scientific research laboratories to synthesize pure hydrocarbons of high molecular weight and to determine the physical constants of these substances. Such data, now extremely rare, will be of incalculable aid in identifying the pure hydrocarbons which it is hoped will be isolated from the lubricating oil fraction of petroleum.

PHYSICO-CHEMICAL METHODS OF FRACTIONATION

The work Institute Research Project 6 on the resolution of the naphtha fraction of petroleum into its major hydrocarbon constituents has demonstrated the prac-

*These data were assembled by B. J. Mair.

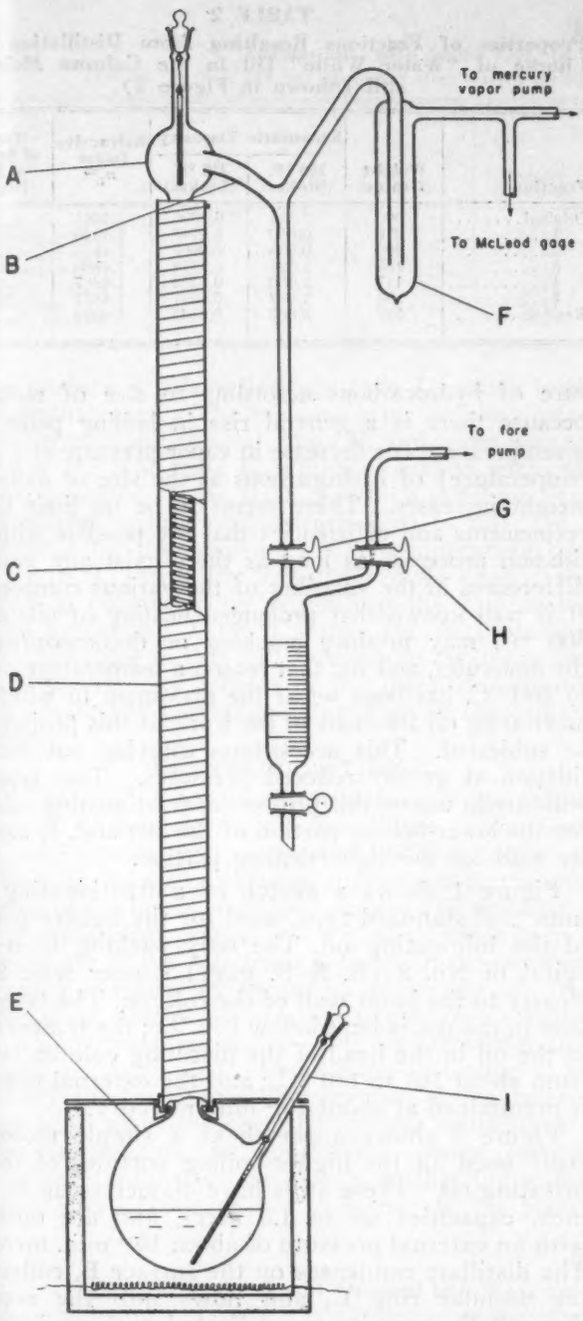

FIGURE 1

Fractionating Column for Distilling Lubricating Oil in Vacuum

***A*, bulb serving as a condenser; *B*, conduit to receiver and high-vacuum system; *C*, fractionating column with copper spiral; *D*, electrically-heated jacket; *E*, still pot; *F*, liquid-air trap; *G*, *H*, stopcocks permitting withdrawal of sample without breaking vacuum in still; *I*, tube for introducing charge.**

ticability and usefulness of four physico-chemical fractionating tools: distillation, crystallization, extraction, and adsorption. It has been found that the most effective system of separation consists in the proper interlocking of these methods and the appropriate variation and combination of them to suit the particular fraction under investigation.

In the investigation of the lubricating oil fraction these same methods of fractionation are being used with gratifying success—although they are, of course, carried out under conditions widely different from those employed in fractionating the naphtha fraction because of the greatly different size and increased complexity of the molecules. The hydrocarbons in the lubricating oil fraction contain, on the average, about four or five times as many atoms per molecule as those in the gasoline fraction; and the number of possible isomers of triacontane, $C_{30}H_{62}$, is about four billion, which is to be compared with 18 possible isomers of octane, C_8H_{18}.

As has already been pointed out, the petroleum industry has been using these same processes of distillation, crystallization, extraction, and adsorption—in some form or another—for many years; and practically all the lubricating oil that is produced today is derived by a combination of at least three of these four methods of fractionation. The novelty that has been introduced into these fundamental principles and methods of fractionation by the work of Institute Research Project 6, and others whose aim is the separation of petroleum into constituents, has been to refine, adapt, and vary them to solve particular problems more effectively.

The following is a brief description of these fractionating methods as applied to the lubricating oil fraction of petroleum by Institute Research Project 6.

DISTILLATION

Fractional distillation appears to be the most useful and practical means for separating any complex mix-

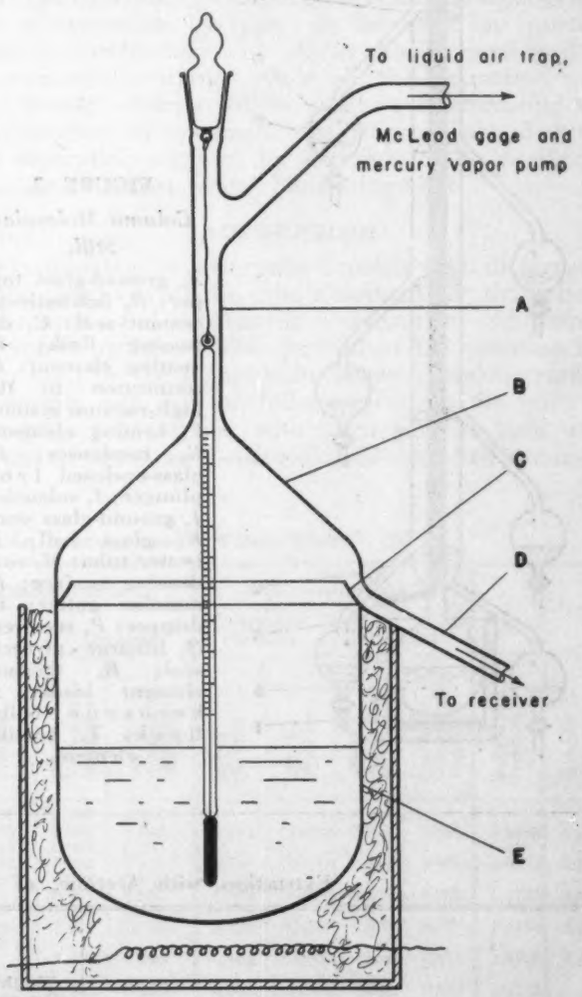

FIGURE 2

Molecular Still for Lubricating Oil.

***A*, tube for introducing charge; *B*, condensing surface; *C*, annulus for collecting condensate; *D*, conduit to receiver; *E*, still pot.**

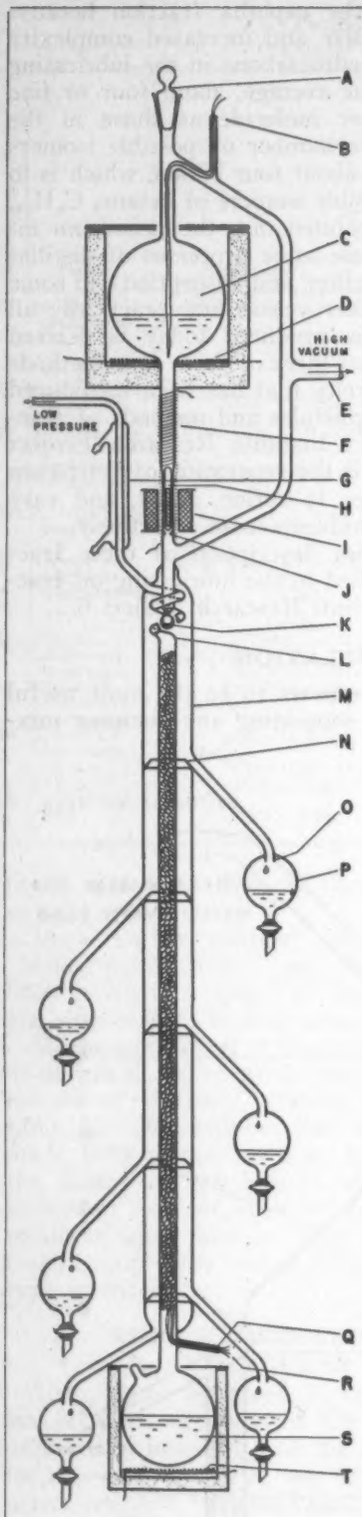

FIGURE 3

Column Molecular Still.

***A*, ground-glass topper; *B*, deKhotinsky cement seal; *C*, degassing flask; *D*, heating element; *E*, connection to the high-vacuum system; *F*, heating element; *G*, condenser; *H*, glass-enclosed iron plunger; *I*, solenoid; *J*, ground-glass seat; *K*, glass ball; *L*, heater tube; *M*, condensing surface; *N*, annular gutter; *O*, dripper; *P*, receiver; *Q*, litharge - glycerin seal; *R*, thermo-element leads; *S*, kerosene boiler flask; *T*, heating element.**

TABLE 2

Properties of Fractions Resulting from Distillation of a Charge of "Water White" Oil in the Column Molecular still (Shown in Figure 3)

Fraction	Weight (Grams)	Kinematic Viscosity		Refractive Index n_D^{25}	Temp. of Section of Still (Deg. C.)
		100 °F. (Stokes)	210 °F. (Stokes)		
Original	900	1.134	0.1096	1.4861	....
1	219	0.650	0.0747	1.4840	214
2	202	0.966	0.0967	1.4852	214
3	150	1.321	0.1171	1.4860	214
4	117	1.650	0.1351	1.4867	218
5	84	1.987	0.1537	1.4875	228
Residue	127	3.067	0.2165	1.4901	...

ture of hydrocarbons according to size of molecule, because there is a general rise in boiling point at a given pressure (or decrease in vapor pressure at a given temperature) of hydrocarbons as the size or molecular weight increases. There seems to be no limit to the refinements and efficiencies that are possible with distillation processes as long as there exist any practical differences in the volatility of the various components. It is well known that prolonged heating of oils above 300 °C. may produce cracking or decomposition of the molecules, and for that reason a temperature of 250 to 260 °C. has been set as the maximum to which the lubricating oil fractions in the work of this project may be subjected. This necessitates carrying out the distillation at greatly reduced pressures. Two types of stills are in use on this project: *a*, fractionating columns for the lower-boiling portion of the oil; and, *b*, molecular stills for the higher-boiling portion.

Figure 1 shows a sketch of a fractionating column[20], of standard type, used for the lighter portion of the lubricating oil. The only packing in it is a spiral of No. 8 (B. & S. gage) copper wire fitted closely to the inner wall of the column. The temperature in the pot is kept below 260 °C.; the temperature of the oil in the head of the distilling column ranges from about 160 to 190 °C.; and the external pressure is maintained at about 10^{-4} mm. mercury.

Figure 2 shows a sketch of a simple molecular still[20] used for the higher-boiling portions of the lubricating oil. These stills have diameters up to five-inch, capacities up to 1.5 liters, and are operated with an external pressure of about 10^{-4} mm. mercury. The distillate condenses on the surface **B**, collects in the annular ring **C**, and flows into the receiver through **D**. Samples are collected without breaking the vacuum.

Figure 3 shows a column molecular still[20] used for the heavier oil fractions. The pressure external to the distilling zone is maintained at about 10^{-4} mm. mercury. The charge is placed into **C**, where it is pre-heated and completely evacuated, and the oil is then permitted to flow at an approximate rate through the magnetically controlled valve **H** to the

TABLE 3

Extraction, with Acetone, of a "Water white" Distillation Fraction

	Weight (Percent)	Refractive Index n_D^{25}	KINEMATIC VISCOSITY		SAYBOLT UNIVERSAL VISCOSITY		Viscosity Index
			100° F. (Stokes)	210° F. (Stokes)	100° F. (Seconds)	210° F. (Seconds)	
Original	100	1.4728	0.3693	0.0546	175.8	44.3	93
First extract	12.17	1.4764	0.4174	0.0582	198.2	45.4	87
Second extract	12.42	1.4746	0.4027	0.0578	191.3	45.3	93
Third extract	27.85	1.4722	0.3766	0.0557	179.2	44.6	94
Fourth extract	27.51	1.4705	0.3596	0.0548	171.2	44.3	97
Raffinate	20.05	1.4682	0.3343	0.0546	159.7	44.3	111

TABLE 4

Adsorption, with Silica Gel, of a "Water White" Distillation Fraction

(100 ml. oil plus 150 ml. petroleum ether passed through a column containing 150 g. silica gel. at room temperature)

	Weight (Grams)	Refractive Index n_D^{25}	KINEMATIC VISCOSITY		SAYBOLT UNIVERSAL VISCOSITY		Viscosity Index
			100° F. (Stokes)	210° F. (Stokes)	100° F. (Seconds)	210 °F. (Seconds)	
Original	....	1.4734	0.3917	0.0577	186.3	45.2	95
First fraction	15.65	1.4702	0.3565	0.0564	169.8	44.8	107
Second fraction	11.60	1.4717	0.3823	0.0569	181.8	45.0	98
Third fraction	13.44	1.4718	0.3868	0.0571	183.9	45.0	96
Fourth fraction	13.73	1.4718	0.3862	0.0572	183.6	45.1	97
Fifth fraction	10.47	1.4720	0.3871	0.0573	184.0	45.1	97
Silica-gel "hold up"	13.29	1.4819	0.4732	0.0622	224	46.7	84

outer surface of the cylindrical tube **L**, which is the evaporating area. The oil condenses on the surface **M**, collects in the annular rings **N**, and flows into the receiver **P**. The tube **L**, which is packed with jack chain, is sealed to the flask **S**, which contains kerosene whose boiling temperature (200 to 250 °C.) is controlled by the pressure. The temperature drop (about 15 °C.) from top to bottom of the evaporating surface is controlled by regulating the composition of the kerosene. Table 2 shows the data obtained in fractionating in this still a charge of "water white" oil. The viscosity indices of the fractions obtained were practically unchanged from that of the original charge.

CRYSTALLIZATION

The process of fractional crystallization operates by virtue of differences in the composition of the liquid and solid phases, just as fractional distillation is dependent for its operation upon differences in the composition of the liquid and vapor phases. The principle of the crystallization process has for many years been in common use in the petroleum industry in the dewaxing process. For liquids as viscous as lubricating oils fractionation by simple refrigeration is not very efficient, and is sometimes impossible—and crystallization from solvents must be used. In addition to having a low solubility for the desired hydrocarbon at the freezing temperature and an appreciably greater solubility at a higher temperature, an appropriate solvent provides the proper fluidity for the system so that the wanted crystals have a good chance to form. In the present work crystallization from a solvent was used to effect a separation of the "wax" from the original crude oil,[20] and subsequently it will be used on a smaller scale to fractionate the cuts obtained by systematic distillation.

EXTRACTION

Fractionation by extraction is a method being developed very extensively by the industry for processing lubricating oil, because that method has particular advantages for fractionating lubricating oil stock. Whereas distillation separates with respect to size of molecule or molecular weight, extraction can, by means of appropriate solvents, be used to separate with respect to both size and type of molecule—although it is usually most effective in separation by type. In the work on Institute Project 6 extraction with sulfur dioxide was used to fractionate the original crude oil, and extraction with appropriate solvents will be used in fractionating the cuts obtained by systematic distillation. Table 3 shows the separation obtained by extracting with acetone a fraction of "water white" lubricating oil.[20]

ADSORPTION

Fractionation by adsorption depends upon differences in the selectivity of the solid absorbent for the various components, and is primarily a separation with respect to type of molecule. This method of fractionation has been used by the industry for many years in treating crude oils with clay or fuller's earth. In the work of this project adsorption with silica gel has been used on the dewaxed and sulfur-dioxide-extracted crude oil

TABLE 6

Physical Properties of Original Oil, Wax, Sulfur-Dioxide Extract, and "Water White" Oil

Cut No.	Original Oil: Kinematic Viscosity 150 °F. (Stokes)	Original Oil: Kinematic Viscosity 210 °F. (Stokes)	Original Oil: Density 150 °F. (Grams per Milliliter)	Original Oil: Density 210 °F. (Grams per Milliliter)	Wax: Kinematic Viscosity 150 °F. (Stokes)	Wax: Kinematic Viscosity 210 °F. (Stokes)	Wax: Density 150 °F. (Grams per Milliliter)	Wax: Density 210 °F. (Grams per Milliliter)	Sulfur-Dioxide Extract: Kinematic Viscosity 100 °F. (Stokes)	Sulfur-Dioxide Extract: Kinematic Viscosity 210 °F. (Stokes)	Sulfur-Dioxide Extract: Density 100 °F. (Grams per Milliliter)	Sulfur-Dioxide Extract: Density 210 °F. (Grams per Milliliter)	"Waterwhite Oil": Kinematic Viscosity 100 °F. (Stokes)	"Waterwhite Oil": Kinematic Viscosity 210 °F. (Stokes)	"Waterwhite Oil": Density 100 °F. (Grams per Milliliter)	"Waterwhite Oil": Density 210 °F. (Grams per Milliliter)	Refractive Index n_D^{25}	Weight (Grams)
23	0.094	0.0460	0.854	0.835	0.0615	0.0330	0.783	0.761	1.89	0.0807	0.989	0.948						
24	0.103	0.0452	0.856	0.836	0.0705	0.0354	0.794	0.773	1.72	0.0828	0.987	0.963	0.214	0.0422	0.849	0.804	1.4684	3,134
25	0.113	0.0480	0.858	0.837	0.0735	0.0379	0.799	0.779	2.60	0.0915	0.983	0.950						
26	0.119	0.0523	0.859	0.839	0.0825	0.0400	0.800	0.780	2.72	0.0942	0.983	0.956	0.257	0.0465	0.847	0.802	1.4704	2,512
27	0.128	0.0536	0.860	0.840	0.0822	0.0410	0.800	0.781	4.12	0.113	0.992	0.958						
28	0.138	0.0575	0.862	0.842	0.0893	0.0473	0.805	0.784	4.57	0.125	0.991	0.955	0.300	0.0498	0.850	0.809	1.4709	2,944
29	0.138	0.0583	0.863	0.843	0.0902	0.0518	0.805	0.786	6.79	0.137	1.013	0.982						
30	0.143	0.0588	0.859	0.839	0.0925	0.0457	0.804	0.783	3.37	0.118	0.971	0.932	0.328	0.0547	0.850	0.821	1.4733	2,189
31	0.176	0.0687	0.865	0.844	0.104	0.0498	0.813	0.792	191	0.359								
32	0.213	0.0828	0.870	0.850	0.118	0.0555	0.812	0.792	.....	.....	1.067	0.990	0.409	0.0604	0.857	0.831	1.4739	2,214
33	0.256	0.104	0.873	0.856	0.131	0.0777	0.819	0.799	28.5	0.268								
34	0.311	0.108	0.877	0.857	0.173	0.0736	0.826	0.806	.....	.....	0.993	0.950	0.591	0.0785	0.856	0.819	1.4743	1,608
35	0.329	0.114	0.879	0.859	0.187	0.0785	0.829	0.810	64.7	0.383								
36	0.446	0.146	0.884	0.865	.....	0.0835	.....	0.807	.....	.....	1.007	0.960	0.757	0.0882	0.860	0.825	1.4771	958
37	0.557	0.160	0.886	0.867	.....	0.0976	.....	0.817	384	0.712								
38	0.648	0.187	0.891	0.870	.....	0.1102	.....	0.818	.....	.....	1.032	0.970	0.824	0.0952	0.862	0.825	1.4772	505
a	From silica gel hold-up points (See text and Fig. 4.)				23-28				2.80	0.122	0.972	0.955	0.605	0.0715	0.878	0.841	1.4909	1,423
b					29-32				6.60	0.187	0.967	0.936	0.584	0.0769	0.866	0.826	1.4815	595
c					33-38				8.78	0.255	0.949	0.912	1.13	0.1096	0.873	0.845	1.4861	1,693
					Total wax=20.25 kg.				Total extract=17.93 kg.				Total "waterwhite" oil=1978. kg.					

TABLE 5

Physical Data on the Lubricating Fractions of Crude from South Ponca Field, Kay County, Oklahoma

	Wax Distillate	Residuum
Yield, percent of crude	18.1	10.2
Gravity, deg. API	29.4	18.1
Flash point, ° F.	325	545
Fire point ° F.	390	620
Viscosity, Saybolt seconds at:		
100° F.	106	...
210° F.	...	207
Pour point, ° F.	80	92

in order to obtain a "water white" fraction. Silica gel has been found to be very effective in removing aromatic constituents from the naphtha fraction,[22] and it is believed that this adsorbent will be useful in fractionating the cuts obtained from the systematic distillation of the lubricating oil. Table 4 shows the results obtained by subjecting a sample of "water white" oil to adsorption with silica gel.[20]

PRELIMINARY FRACTIONATION OF A MID-CONTINENT OIL

The actual fractionation of the lubricating oil portion of a Mid-Continent petroleum was begun by Institute Research Project 6 about January, 1934, and a report of the results obtained to date have been completed by Mair, Schicktanz, and Rose.[20]

The physical data on the wax distillate and residuum of the original crude oil[1] are given in Table 5. The oil was distilled in vacuo by Sun Oil Company, and then shipped to the National Bureau of Standards in tightly-sealed metal containers, in an atmosphere of nitrogen. Sixteen of these fractions (designated as cuts 23 to 38) with a total weight of about 67 kg. and representing about 9.6 percent of the crude oil, were selected for the primary study. These fractions were dewaxed, extracted with sulfur dioxide, and treated with silica gel in order to obtain, for first investigation, a "water white" portion which was free of wax, sulfur compounds, and asphaltic and resinous substances.

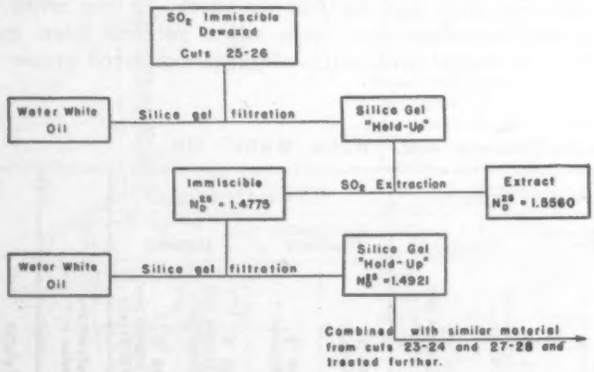
SO_2 Immiscible Dewaxed Cuts 25-26
Water White Oil
Silica gel filtration
Silica Gel "Hold-Up"
Immiscible N_D^{20} = 1.4775
SO_2 Extraction
Extract N_D^{20} = 1.5560
Water White Oil
Silica gel filtration
Silica Gel "Hold-Up" N_D^{20} = 1.4921
Combined with similar material from cuts 23-24 and 27-28 and treated further.

FIGURE 4

Interlocking Scheme of Separation by Extraction and Adsorption.

Table 6 summarizes the data on the original cuts, the wax, the sulfur-dioxide extract, and the "water white" oil. The values of the viscosity indices for the various fractions ranged as follows: original oil, about 75 to 90; wax, about 125 to 150; sulfur-dioxide extract, about —150 to —300; "water white" oil, about 100 to 120. The wax was removed by using ethylene chloride as a solvent and chilling to —18 °C. The extract was obtained by using sulfur dioxide in batch extractions. In order to remove the remaining sulfur compounds

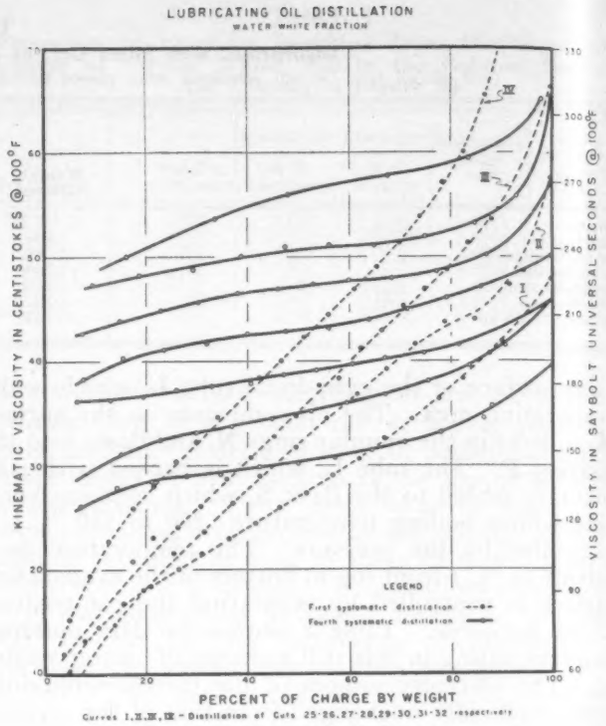

FIGURE 5

Chart Showing the Result of Four Stages of Systematic Distillation of the Lower-Boiling "Water White" Oil.

and the asphaltic and resinous materials, and to obtain a stable "water white" oil, the oil was treated with silica gel after dewaxing and extracting. The data shown in Table 7 indicate that the silica gel as used in

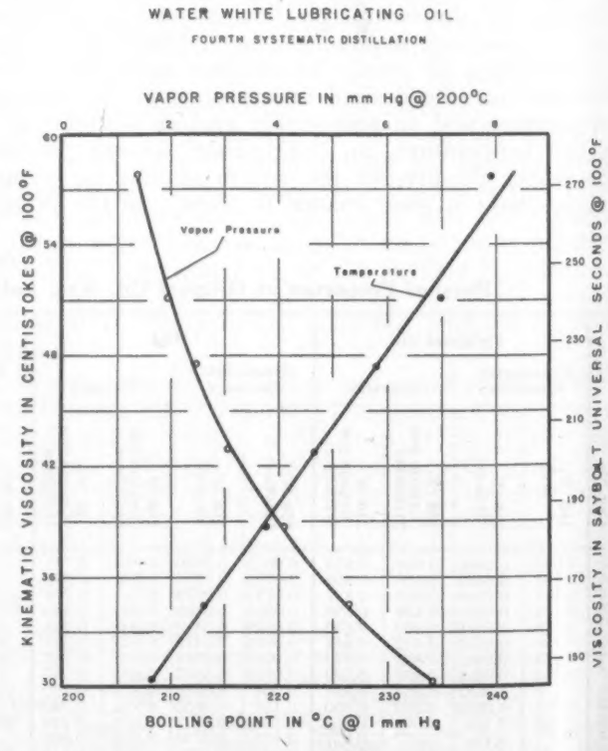
WATER WHITE LUBRICATING OIL
FOURTH SYSTEMATIC DISTILLATION
VAPOR PRESSURE IN mm Hg @ 200°C
Vapor Pressure
Temperature
KINEMATIC VISCOSITY IN CENTISTOKES @ 100°F
VISCOSITY IN SAYBOLT UNIVERSAL SECONDS @ 100°F
BOILING POINT IN °C @ 1 mm Hg

FIGURE 6

Relation between viscosity and boiling point at a given pressure (and vapor pressure at a given temperature) for the middle cut of each of the seven charges of the fourth stage of the distillation of the lower-boiling "water white" oil (see Figure 5).

TABLE 7

Nature of Adsorption with Silica Gel

("Water white" oil passed through 102 g. silica gel at 90 to 100 °C.)

MATERIAL	Weight (Grams)	Refractive Index n_D^{65}	DENSITY		KINEMATIC VISCOSITY	
			150° F. (Grams per Milliliter)	210° F. (Grams per Milliliter)	150° F. (Stokes)	210° F. (Stokes)
Original	311.58	1.4710	0.846	0.824	0.1360	0.05654
Filtrate	246.44	1.4663	0.838	0.815	0.1245	0.0540
Adsorbed material	64.83	1.4899	0.875	0.851	0.1710	0.0653
Re-combination of filtrate with adsorbed material	311.27	1.4710	0.846	0.825	0.1361	0.05657

these experiments did not crack nor polymerize the hydrocarbons. Figure 4 illustrates the interlocking process used at this stage in order to obtain the maximum amount of "water white" oil.

The "water white" oil was then fractionally dis-

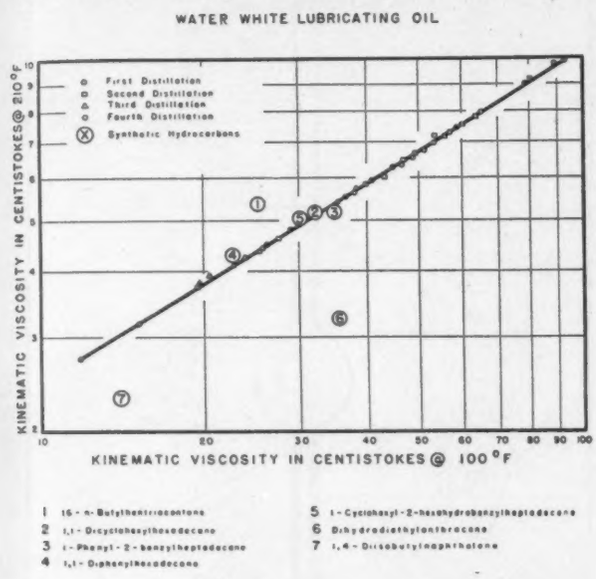
WATER WHITE LUBRICATING OIL
KINEMATIC VISCOSITY IN CENTISTOKES @ 210°F
KINEMATIC VISCOSITY IN CENTISTOKES @ 100°F
First Distillation
Second Distillation
Third Distillation
Fourth Distillation
Synthetic Hydrocarbons
1 16 - n- Butylheptriacontane
2 1,1 - Dicyclohexylhexadecane
3 1 - Phenyl - 2 - benzylheptadecane
4 1,1 - Diphenylhexadecane
5 1 - Cyclohexyl - 2 - hexahydrobenzylheptadecane
6 Dihydrodiethylanthracene
7 1,4 - Dicyclobutylnaphthalene

FIGURE 7

Plot of the logarithm of the viscosity at 210°F. against that at 100°F. for different fractions from various stages of the systematic distillation of the "water white" oil. The numbers represent the values computed for the hydrocarbons listed above.

tilled, the more volatile portion in the column shown in Figure 1, and the less volatile portion in the stills shown in Figures 2 and 3. The results of the systematic distillation of the lighter portion of the "water white" oil through four stages are shown in Figure 5. Because it was more convenient to measure the viscosities of the cuts obtained from the still than their true boiling points, and since it was found that there was a satisfactory relation between viscosities and true boiling points of these cuts, the re-blending up to this stage was done on the basis of viscosity. Figure 6 shows the relation between the viscosity at 100 °F. and the boiling point at 1 mm. mercury (and the vapor pressure at 200 °C.) for the middle cuts from each of the seven charges in the fourth stage of the systematic distillation Figure 5.

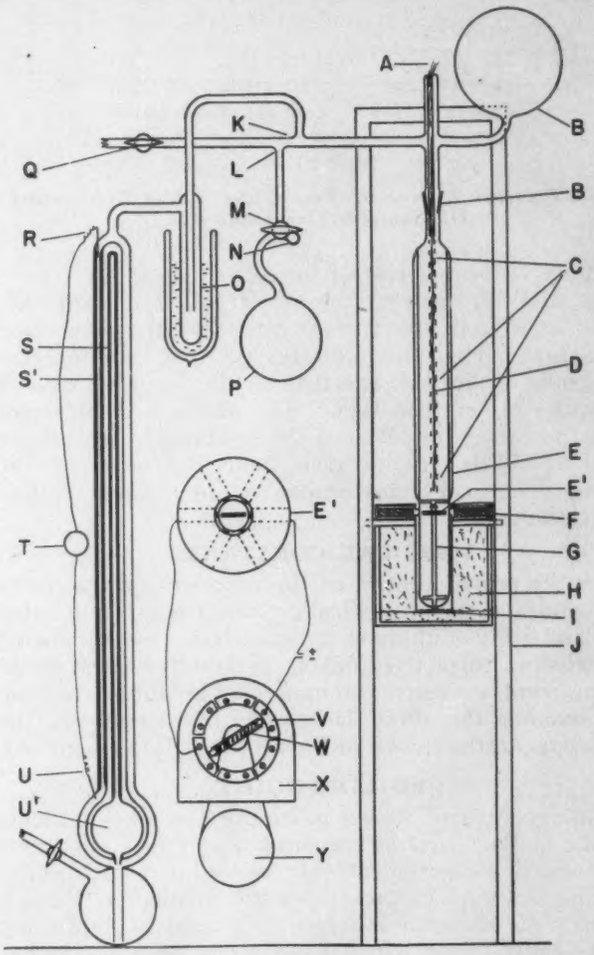

FIGURE 8

Sketch of Apparatus for Measuring the Boiling Points of Lubricating Oils at Reduced Pressures.

***A*, thermo-element leads; *B*, 3-liter ballast flask; *B'*, ground joint; *C*, thermo-elements; *D*, perforated glass-tube; *E*, vacuum jacket; *E'*, glass-enclosed iron rod; *F*, electromagnets; *G*, internal stirrer; *H*, heater box; *I*, heating element; *J*, iron frame; *K*, connection to McLeod gage; *L*, connection to nitrogen flask; *M*, three-way stopcock; *N*, measuring bulb; *O*, trap; *P*, 2-liter flask filled with dry pure nitrogen; *Q*, stopcock between the pumping system and the boiling-point apparatus; *R*, and *U*, tungsten seals; *S* and *S'*, capillary tubes of McLeod gage; *T*, galvanometer; *U'*, McLeod gage; *V*, discontinuous brass ring; *W*, rotor; *X*, commutator; *Y*, variable-speed motor.**

TABLE 8

Relation of Boiling Point to Refractive Index, Viscosity, and Temperature Coefficient of Viscosity, for Two Samples of "Water White" Oil

SAMPLE	Refractive Index n_D^{25}	KINEMATIC VISCOSITY		Boiling Point (at 1 mm. Mercury) (° C.)
		100° F. (Stokes)	210° F. (Stokes)	
I Original "water white" lubricating oil	1.4733	0.3283	0.0547	198
II Tenth (middle) fraction obtained from distillation of *I*	1.4733	0.3279	0.0518	210.5

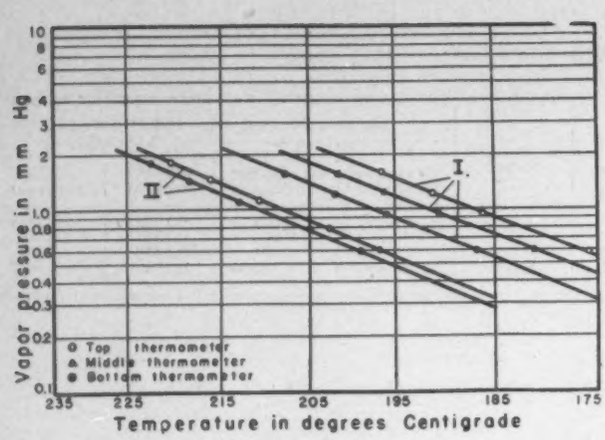

FIGURE 9

Vapor-Pressure Curves of Two Water White Lubricating Oil Samples (see Table 8).

Figure 7 shows a plot of the logarithm of the viscosity at 210 °F. against that at 100 °F. for many different cuts from the various stages of the systematic distillation. This plot indicates that the fractionation was being made, as expected, on the basis of size of molecules rather than type. The numbers on this plot show the values for seven of the synthetic hydrocarbons listed in Table 1, and give some indication of the average chemical constitution of the "water white" lubricating oil.

PHYSICAL CONSTANTS

For the proper control of the processes of fractionation, and for the identification of closely-fractionated cuts and of the ultimate hydrocarbons, measurements of density, refractive index, carbon-hydrogen ratio, boiling point, viscosity, and molecular weight are needed. For making the three last-named measurements the special apparatus shown in Figure 8 has been assembled.

BOILING POINT

The apparatus [23] shown in Figure 8 is used to measure the boiling point at pressures near 1 to 2 mm. mercury. Such measurements are needed for the proper blending of cuts in the systematic distillation. Table 8 shows the differences which may exist in the boiling points of fractions which have about the same values of refractive index, viscosity, and change of viscosity with temperature. This same apparatus permits investigation, to a certain extent, of the purity of various cuts with respect to components of different volatility. Figure 9 illustrates such data.

VISCOSITY

Figure 10 shows a sketch of one of the pipettes[20] used to determine the viscosity of these oils in fundamental units of kinematic viscosity, with an accuracy of about ± 1 percent and a precision of about ±0.2 percent. It is also possible to determine the density at the temperatures at which the viscosity measurements were made, usually 100 °F. and 210 °F.; so that, if necessary, the absolute viscosity can be computed.

MOLECULAR WEIGHT

The molecular weight of the various oil fractions can be determined with the apparatus [24] shown in Figure 11. The determination consists in measuring directly the difference in boiling point of a pure solvent (benzene, for example) and that of a sample of the same solvent to which has been added a weighed amount of the non-volatile oil. This ebullioscopic method of boiling-point elevation gives in this apparatus values of molecular weight accurate to within ± 1 percent. Figure 12 shows some results obtained on a "water white" oil and an "extract" oil. The true values are those given by the extrapolation to zero concentration. Especially for substances of the nature of lubricating oils, the ebullioscopic method of determining molecular weights possesses certain inherent advantages over the cryoscopic method of freezing-point lowering.

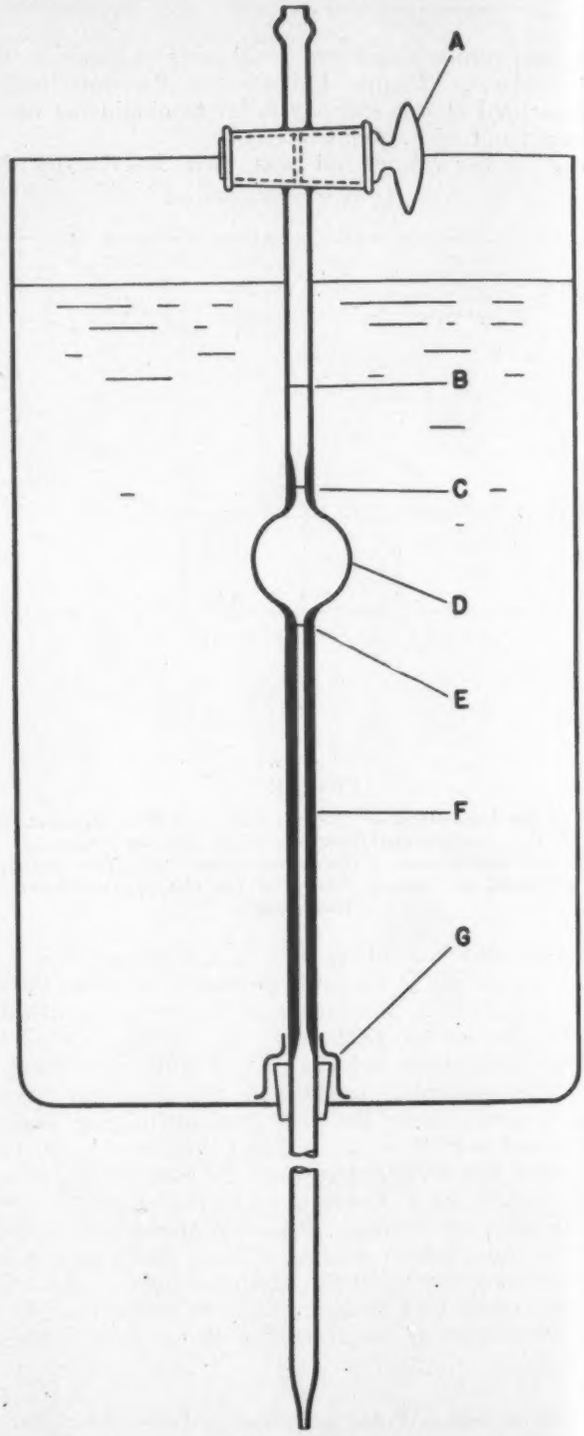

FIGURE 10

Viscosity Pipette.

***A*, stopcock; *B*, etched mark for density determination; *C*, *E*, etched marks for viscosity determinations; *D*, bulb, volume about 5 cc.; *F*, capillary; *G*, glass protecting ring with rubber stopper. The oil bath is controlled to ± 0.05°F. and the air bath to ± 2°F.**

CONCLUSION

Although no definite, pure, individual hydrocarbons have ever been isolated from the lubricating oil fraction of petroleum, the information which has accumulated from the work of all the investigators in this field indicates that the hydrocarbon constituents of the better or more highly refined lubricating oils may include: 1, naphthenes (saturated cyclic) having one or two rings per molecule and long branched side chains; and, possibly, 2, branched-chain paraffins.

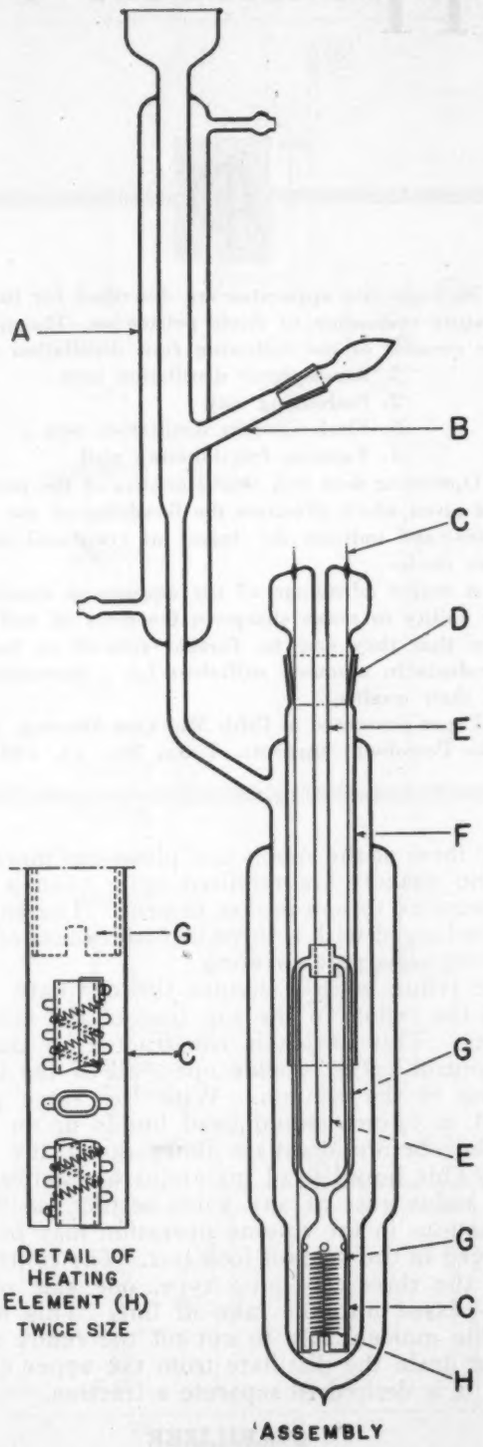

FIGURE 11

Ebullioscopic Apparatus for Determining Molecular Weights of Lubricating Oil Fractions.

***A*, condenser; *B*, tube for introduction of liquid solutes; *C*, tungsten leads; *D*, ground-glass joint; *E*, thermo-element well; *F*, sheath to protect thermocouple from cold liquid from condenser; *G*, bell of pumping apparatus; *H*, resistance heating coil.**

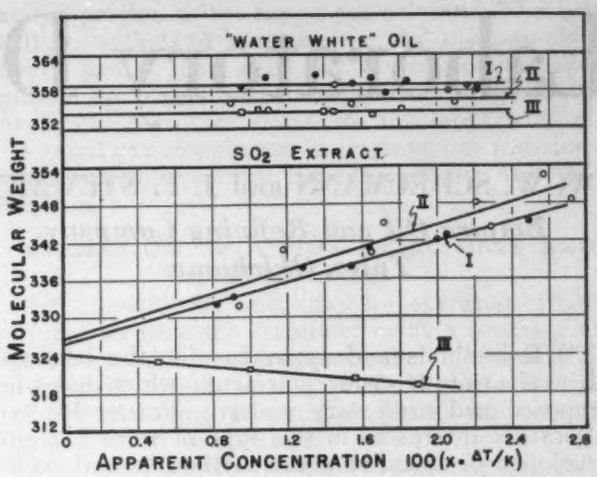

FIGURE 12

Results of Determinations of Molecular Weights of a "Water White" Oil and an "Extract" Oil

***I, II, III*, molecular-weight results in *n*-heptane, 2,2,4-trimethylpentane and benzene, respectively. The true molecular weight is given by the intercept at zero concentration.**

Just as in the case of the naphtha fraction,[1] the most effective separation of the lubricating oil will result from the proper interlocking, combination, and variation of the different methods of fractionation. The first objective of the work of Institute Research Project 6 on the lubricating oil fraction is to separate the oil into close cuts containing molecules of about the same size (or molecular weight or boiling point), and then to subject these cuts to fractionation with respect to type—obtaining fractions which will contain molecules of the same type and size. These isolated fractions will then be identified with respect to size and type of molecule. Once the separation reaches this stage, the way will be made clear for the ultimate separation of pure hydrocarbons.

The knowledge obtained by the project in this work, particularly with regard to the practical separation of the oil into fractions differing both in size and type of molecule, should be of considerable benefit to the industry, which is today vitally concerned with the problem of separating the "good" molecules from the "bad" in the process of making superior lubricating oil from ordinary crude stock.

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Laboratory Distilling Apparatus . . .

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Methods and apparatus are described for the laboratory evaluation of crude petroleum. The apparatus consists of the following four distillation units:

1. **Atmospheric distillation unit**
2. **Stabilizing unit**
3. **Flash vacuum distillation unit**
4. **Vacuum fractionating unit**

Operating data and characteristics of the products are given which illustrate the flexibility of the apparatus, and indicate the degree of fractional separation made.

A major advantage of the equipment consists of its ability to make sharp-cut fractions of sufficient size that they can be further refined to finished products in amounts sufficient for a determination of their quality.

Paper presented at Fifth Mid-Year Meeting, American Petroleum Institute, Tulsa, May 15, 1935.

THE methods and apparatus for the laboratory evaluation of crude petroleum which have been proposed and used vary widely. Practically every laboratory interested in this type of work has either developed or modified some method to suit its own requirements and facilities, so that no standard or universal method of crude evaluation has been developed within the industry.

The American Society for Testing Materials' Method of Test for Distillation of Crude Petroleum (D285-33) makes no pretense of giving more than very meager information concerning the products obtainable from crude oils. Of the other methods which have been proposed, the "true boiling-point" method developed by Beiswenger and Child,[1] and the somewhat similar but more elaborate method developed by Podbielniak[2] are undoubtedly outstanding. Either of these methods provides excellent data for designing or determining the efficiency of commercial distillation equipment, but they do not provide a sufficient quantity of distillate fractions to permit a thorough study of subsequent refining operations and quality of the products obtained.

This paper briefly describes four distillation units which have been used over a period of three years for crude oil and pressure distillate evaluations. Experience has also shown that they are adaptable to almost any type of research or development problem involving separations by distillation.

ATMOSPHERIC FRACTIONAL DISTILLATION

Figure 1 shows the essential parts of the primary distillation unit. It consists of a horizontal still equipped with a 14-plate bubble cap fractionating column, a three-pass tubular-type total condenser, a reflux control device, and a jacketed distillate receiver which may be iced for collecting low-boiling fractions.

The fractionating column was designed to handle a maximum of approximately 90 cubic feet of vapor per hour. This, for the lighter distillates, corresponds to about 12 liters of liquid per hour, of which two to four liters would normally be taken off as distillate and 10 to eight liters returned to the top of the column as reflux. At this rate the vapor velocity through the free space in the column is slightly less than 0.5 feet per second and about 16 feet per second through the bubble cap slots. The column is built in sections, and consists of 14 plates separated by welded flange spools of three-inch pipe. Each spool is three inches in length. Each plate has one centrally located vapor untake and bubble cap, and two downpipes set 90 degrees apart. The downpipes hold a ½-inch liquid level on each plate, and extend ¼-inch below the liquid level of the tray below. Those from the first tray into the still are provided with U seals.

The column sections are bolted together. All flange faces of the spools and plates are machined so that no gaskets are required other than a coating of Permatex form-a-gasket cement. The entire column is lagged with a three-inch thickness of 85 percent magnesia pipe covering.

The reflux control divides the distillate, and returns the reflux to the top tray of the column by gravity. This device is constructed so that when the control valve is wide open, all of the distillate returns to the column. With the valve partially closed, a ½-inch liquid head builds up in the top chamber before distillate flows down the take-off line. This liquid head maintains a practically constant reflux rate at any valve setting, so that any fluctuations in the column operation may be readily observed in the take-off look box. The control valve is of the three-way plug type, one side of which is by-passed into the take-off line. This makes it possible momentarily to cut off the reflux entirely, and to drain the distillate from the upper chamber, when it is desired to separate a fraction.

STABILIZER

The stabilizer was built primarily for use in connection with pressure distillate evaluations. It was designed for the purpose of obtaining a propane-free butane cut as distillate, with pentanes, and heavier, retained as bottoms. Figure 2 shows the essential parts of this unit. The fractionating column consists of four five-foot sections of one-inch extra heavy pipe.

Each section is filled with No. 18 single-jack chain. The condenser and distillate receiver are both connected with an ammonia refrigeration system and cooled by direct expansion. The still is heated with a 1,000-watt electric heater, and is also jacketed for ammonia expansion so that the light bottoms may be chilled before they are withdrawn. The reflux device consists of a double needle valve arrangement for dividing the distillate stream and returning any desired portion to the top of the column. The unit is built to withstand pressures up to 150 pounds per square inch. The still and lower portion of the column are lagged with 85 percent magnesia pipe covering. All other parts are insulated with cork.

A small gas compressor is employed to transfer uncondensed vapors from the atmospheric still to the stabilizer.

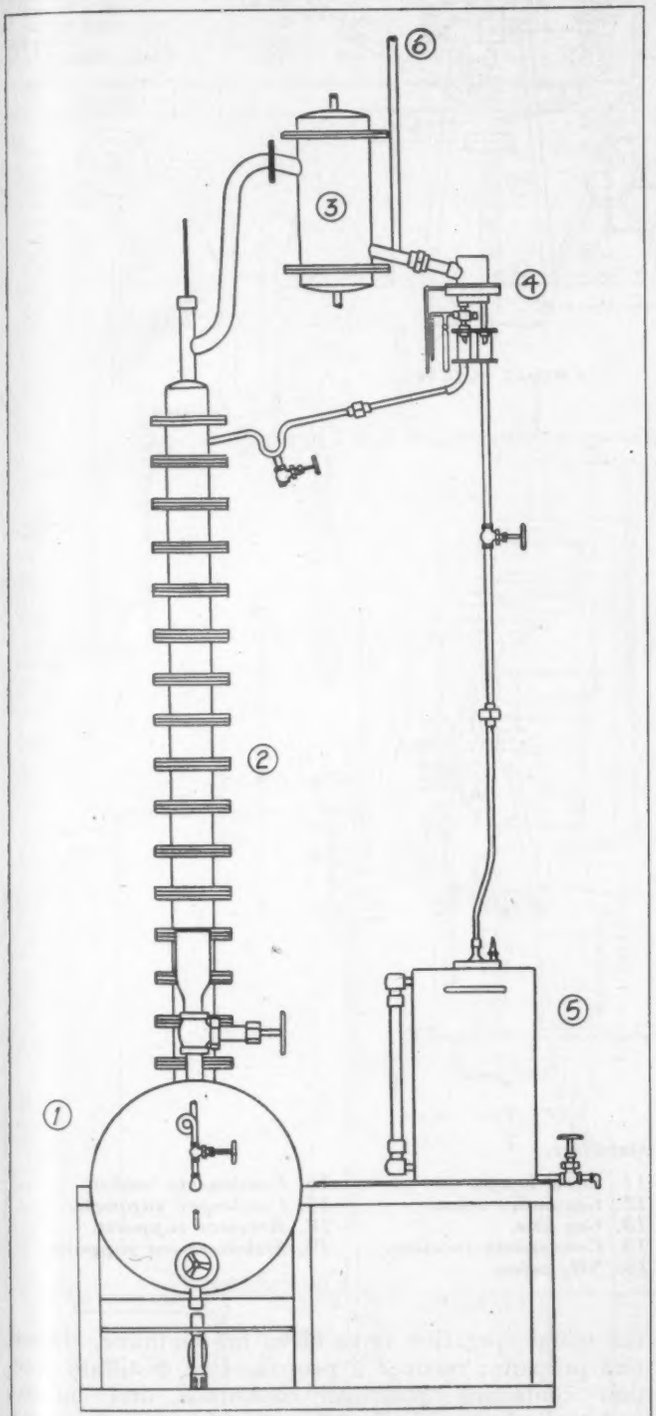

FIGURE 1
Atmospheric Distillation Unit.
1. Still.
2. Fractionating column.
3. Total condenser.
4. Reflux control.
5. Distillate receiver.
6. Vent or connection to stabilizer.

OPERATION OF ATMOSPHERIC UNIT AND STABILIZER

The atmospheric unit may be operated either in conjunction with the stabilizer or as a separate unit. For the evaluation of crude oils the stabilizer is ordinarily used only to condense the lightest fractions, while in rerunning pressure distillates the two units are operated in conjunction.

For crude oil evaluation, approximately five gallons of the crude is measured or weighed into the atmospheric still. In order to avoid loss of low boiling constituents, all vents from the unit are closed and the reflux control set for total reflux during the initial heating period. Heat is then applied to the still, and uncondensed vapors are pumped over into the stabilizer still—which is cooled to —20°F. The compressor operation is regulated so that the pressure on the atmospheric still is held under one pound per square inch, gage. Operation in this manner is continued until the temperature at the top of the column reaches 110°F. At this point cooling water is turned into the condenser, the connection to the stabilizer is closed, and the atmospheric still vented. Distillation then proceeds in the usual manner, with the reflux control set to return about three fourths of the distillate to the column as reflux. The light distillates condensed in the stabilizer are blended back with the first fraction taken from the atmospheric still.

Fractions generally are separated at 50°F. intervals between 250 and 450°F. At each cut point the column is allowed to operate on total reflux for a short period. This concentrates the lowest boiling constituents at the top of the column, which are removed as distillate until the temperature at the top of the column remains constant at the cut temperature—with the column operating on total reflux. Reasonably sharp separations are obtained in this manner.

The distillate fractions obtained from this distillation are blended to obtain the various commercial grades of gasoline. Sufficient quantities of each grade then are available for determination of octane number, treating requirements, and other pertinent data.

The evaluation of pressure distillates is somewhat more involved. In our work along this line, pressure-distillate samples generally are collected in steel drums, under a pressure of about 50 pounds per square inch, directly from the accumulator of the cracking unit. These cylinders are suspended above the atmospheric still, and connected with the charging line by flexible steel tubing. The charge is then gradually released into the still, and all uncondsensed vapors are pumped over into the stabilizer. The weight of the charge is determined by the loss in weight of the cylinder.

During the initial heating period additional vapors are pumped over into the stabilizer until the temperature at the top of the atmospheric column reaches 110°F., and no pressure is built up on the atmospheric still with the column operating on total reflux. The atmospheric unit then is vented, and distillation con-

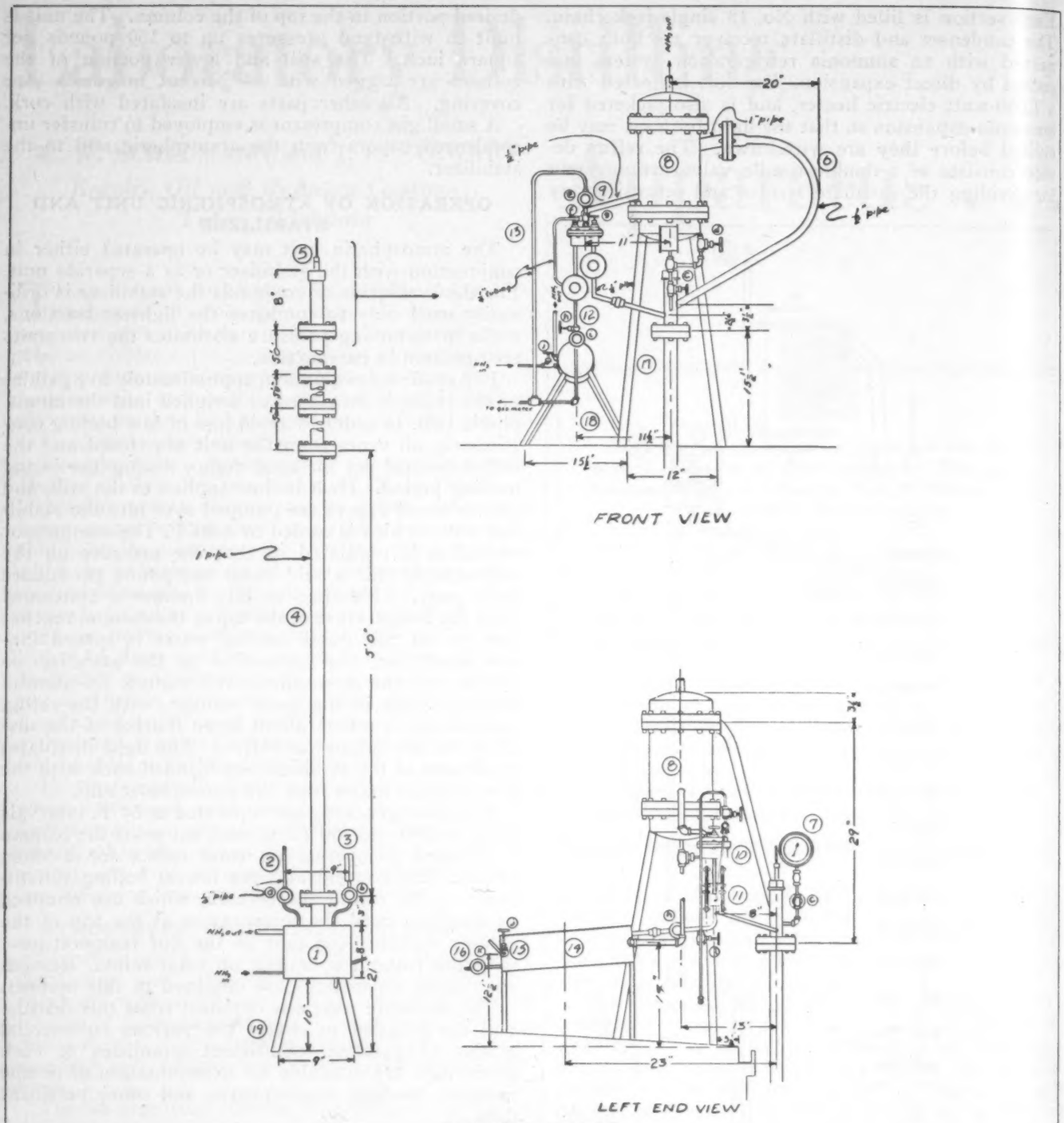

FIGURE 2 *Stabilizer.*

1. Stabilizer pot.	*6. Vapor line.*	*11. Look boxes.*	*16. Condensate outlet.*
2. Feed line.	*7. Pressure gage.*	*12. Gas-outlet valve.*	*17. Condenser supports.*
3. Pressure gage.	*8. Condenser.*	*13. Gas line.*	*18. Receiver supports.*
4. Stabilizer column.	*9. Condensate line.*	*14. Condensate receiver.*	*19. Stabilizer-pot supports.*
5. Thermometer.	*10. Reflux regulator.*	*15. NH_3 valve.*	

tinued in the same manner as described for crude oil evaluation.

The charge in the stabilizer unit at this point consists principally of methane, ethane, propane, butanes, and pentanes, together with a small percentage of air and heavier hydrocarbons. Varying percentages of unsaturated hydrocarbons containing the same number of carbon atoms also are present, and further reference to the normal hydrocarbons will include the unsaturated members boiling in the same range. While this unit may be utilized for various purposes, the usual operation is to bleed off methane, ethane, and propane; recover a propane-free distillate fraction containing principally *iso*butane and butane; and retain butane-free pentanes and heavier bottoms.

With the charge in the stabilizer, the pressure on the unit is usually about 100 pounds per square inch. The condenser is cooled to —35°F., and heat applied to the still. All condensed distillate is returned to the column as reflux. After a short period of refluxing the temperature at the top of the column comes to equilibrium at or below the boiling point of propane

TABLE 1

Distillation—A.S.T M. D86-30:	Top-Column Temperature at Cut Point				
	200 °F.	250 °F.	300 °F.	350 °F.	Residue
	°F.				
Initial boiling point	147	208	258	310	364
10 percent point	158	214	264	313	370
20 percent point	160	216	266	314	372
30 percent point	162	217	268	317	376
40 percent point	164	220	270	318	378
50 percent point	168	222	272	320	382
60 percent point	171	224	276	324	386
70 percent point	176	228	278	326	390
80 percent point	182	234	283	331	398
90 percent point	192	240	291	338	408
End point	208	252	306	354	446
Yield of fractions, percent	20.7	20.8	21.1	19.7	17.7

TABLE 2

	Pressure-Distillate Charge	Butane Cut	Stabilizer Bottoms	Stabilized Pressure Distillate
	Percent			
Hydrocarbon:				
Methane	0.40	...	...	...
C_2 compounds	2.10	...	...	...
C_3 compounds	6.34	0.00	0.00	0.00
C_4 compounds	7.30	100.00	13.91	0.00
Butylene	...	34.50	...	...
Isobutane	...	8.08	...	...
n-butane	...	57.42	...	...
C_5 compounds	7.43	0.00	70.64	5.32
C_6 compounds	8.61	...	11.98	6.89
Residue	67.92	...	3.47	87.79

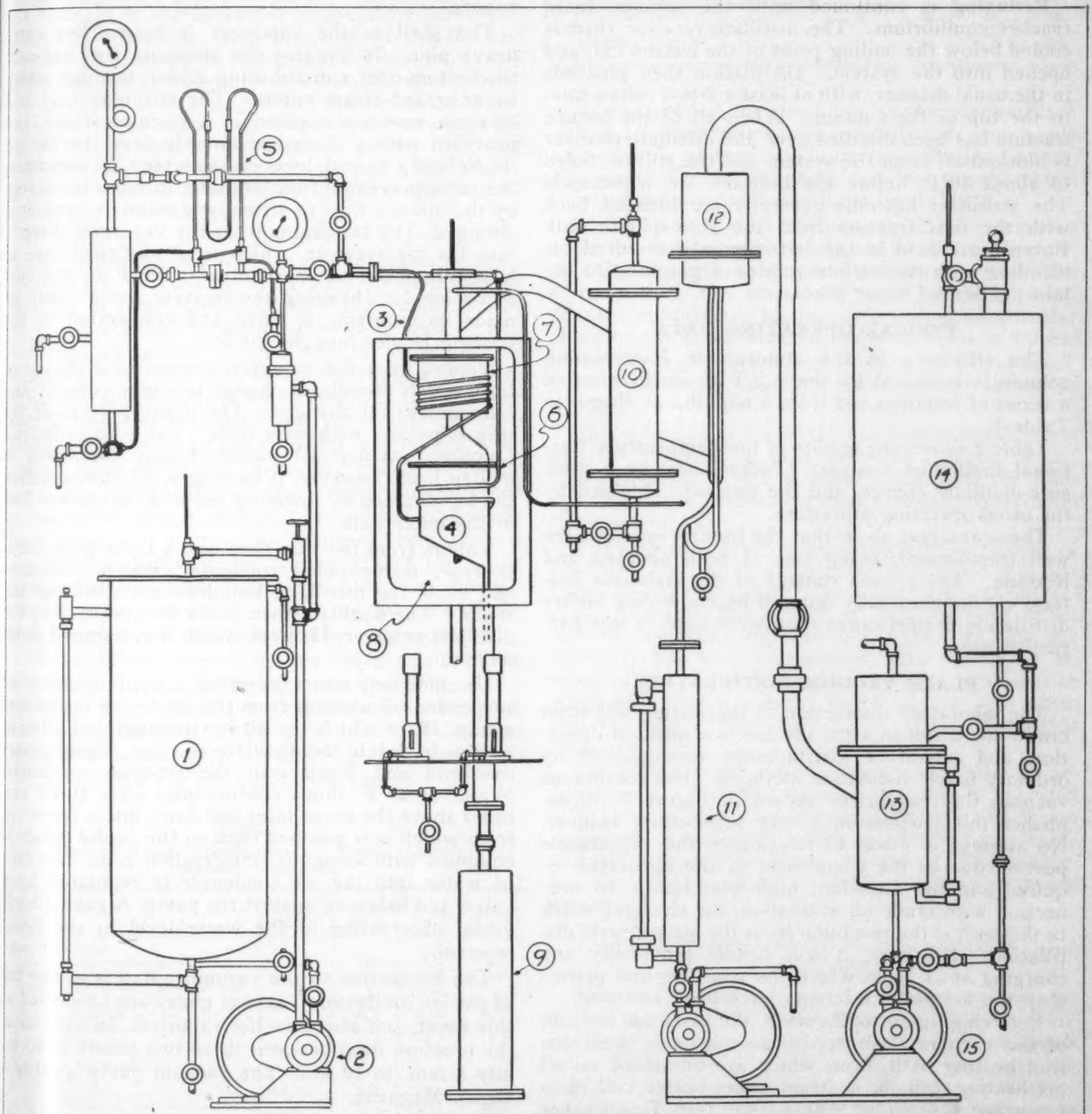

FIGURE 3

Vacuum Flash Distillation Unit

1. Feed tank.
2. Feed Pump.
3. Pre-heater coil.
4. Evaporator.
5. Steam flow meter.
6. Steam super-heater coil.
7. Spray trap.
8. Lead bath.
9. Tar receiver.
10. Distillate condenser and cooler.
11. Distillate receiver.
12. Trap.
13. Jet condenser.
14. Water cooler.
15. Water-circulating pump.

corresponding to the system pressure. With liquid propane refluxing to the top of the column, the system pressure is gradually reduced by bleeding off uncondensed methane and ethane from an outlet above the reflux control through a wet test meter at the rate of approximately 0.1 cubic foot per minute. Propane is then bled from the system in the same manner. The density of the gas being bled off is checked at intervals of 0.5 cubic foot to serve as an approximate check on the operation. The cut point between propane and butanes is sharp, being indicated by an abrupt drop in pressure and rapid rise in temperature at the top of the column.

Refluxing is continued until the column again reaches equilibrium. The distillate receiver then is cooled below the boiling point of the butane cut, and opened into the system. Distillation then proceeds in the usual manner, with at least a 2-to-1 reflux ratio to the top of the column. When all of the butane fraction has been distilled over, the distillate receiver is blocked off from the system and the still is cooled to about 40°F. before the bottoms are withdrawn. The stabilizer bottoms generally are blended back with the first fraction from the atmospheric still. Butanes are held in the receiver until required for blending with the various grades of gasolines to obtain the desired vapor pressure.

TYPICAL OPERATING DATA

The efficiency of the atmospheric fractionating column is indicated by the A.S.T.M. distillations of a series of fractions cut from a naphtha as shown in Table 1.

Table 2 shows the results of low temperature fractional-distillation analyses (Podbielniak) on a pressure-distillate charge, and the products obtained by the usual operating procedure.

These analyses show that the butane cut has been well fractionated, being free of both propane and pentane. The butane content of the stabilizer bottoms can be materially reduced by employing higher distillation temperatures than were used in this particular run.

FLASH VACUUM DISTILLATION

The laboratory distillation of lubricating oils from crude oils down to a tar residue is a difficult operation, and cannot be satisfactorily accomplished by ordinary batch distillation methods. The continuous vacuum flash vaporizer shown in Figure 3 accomplishes this purpose in a very satisfactory manner. No attempt is made to fractionate the vaporizable portion due to the complexity of the apparatus required and the attendant high heat losses. In connection with crude oil evaluation, the charging stock to this unit is the residuum from the atmospheric distillation. However, it will handle practically any charging stock from which the gasoline, and preferably the kerosene, fractions have been removed.

Referring again to Figure 3, the essential features of the vacuum flash apparatus consist of a molten lead heating bath, **8**, in which are immersed an oil pre-heating coil, **3**, a steam super-heater coil, **6**, a vaporizer, **4**, provided with a spray trap, **7**, and vapor and residuum outlets; a distillate condenser and cooler, **10**, a distillate spray trap, **12**, and a steam condenser, **13**. Auxiliary equipment includes a feed tank, **1**, separate receivers for tar, **9**, distillate, **11**, and condensed steam, **14**, together with necessary pumps, gages, and connections.

The feed tank is steam-jacketed so that the charge may be pre-heated to approximately 250°F. to insure uniform flow through the charging valve. The feed pump, **2**, which is a 30 gallon per hour gear pump, circulates the charge continuously through a pressure-relief valve set at 25 pounds per square inch. This holds a constant head against a needle valve through which the charge is metered into the pre-heater coil. The pre-heater coil is a 10-foot length ⅛-inch outside diameter by 5/64-inch inside diameter seamless steel tubing. It enters the vaporizer as shown, and is cut off at an angle of 45 degrees on the inside to produce a tangential motion of the flashing vapors.

The shell of the vaporizer is four-inches extra heavy pipe. It contains one stripping tray set near the bottom over a distributing spider, through which super-heated steam enters. The stripping tray is a 40-mesh screen supported in a circular frame, and provided with a downpipe directly over the tar leg set to hold a ⅜-inch level on the screen. In operation, the tar is prevented from draining through the screen by the upward flow of steam, and intimate contact is obtained. The tar drains from the vaporizer directly into the tar receiver, which is of sufficient size to hold all of the tar normally obtained in one run. Provision for changing the receiver could easily be made by inserting a valve and connection to the vacuum header into the tar line.

Vapors from the vaporizer ascend into the spray trap, which provides a change in vapor velocity and four directional changes. The upper portion of the trap is packed with wire coils. The trap ordinarily functions satisfactorily when totally immersed in molten lead; however, if necessary, additional reflux can be obtained by lowering the level of molten lead in the outer bath.

Vapors from the trap flow into a three-pass, tubular-type, water-cooled condenser, which condenses and cools the distillate, but does not condense the steam. The distillate then flows by gravity into the distillate receiver, **11**, from which it is pumped at intervals.

Uncondensed steam, carrying a small quantity of suspended oil, ascends from the condenser outlet into a trap, **12**, in which the oil is separated and allowed to flow back into the distillate receiver. Steam passes overhead and down into the jet-type condenser. Water at 40°F. flows continuously over three cascades above the vapor inlet and down into a reservoir, from which it is pumped back to the cooler which is equipped with ammonia-refrigeration coils. The flow of water into the jet condenser is regulated by a valve, and balanced against the pump. A gage affords visual observation of the water level in the lower reservoir.

The connection to the vacuum pump is at the top of the jet condenser. Vacuum gages are connected at this point, and also into the vaporizer. In operation, the pressure drop between these two points is normally 8 mm. to 10 mm. The vacuum pump used is a Cenco Megavac.

The heating bath holds approximately 600 pounds of lead. It is heated by four Fisher-Meker-type gas burners. From 2½ to 3 hours are required to melt this volume of lead and bring it up to operating temperature. Any temperature between 650 and 1000°F. may be held easily within a range of 5°F. or less,

and wide temperature fluctuations in the vaporizing section are impossible due to the large volume of lead. At the end of each run the lead is drained into a vat, and ladled into bar molds of such size that the bars may be placed back into the heating bath for re-melting. About 30 minutes are required for this operation.

The operation of the unit is relatively simple; and once it is adjusted to the desired operating conditions, it remains very constant—with little attention other than to pump out the distillate as it is collected. No re-cycling of products is necessary at the beginning of the run, since all parts of the vaporizing section are brought to the operating temperature before the charge is admitted. The character of the tar and percentage of distillate which will be obtained at any given temperature and pressure vary, of course, with the character of the charge and the steam ratio employed. After some experience in operating the unit, it is possible to estimate the proper operating conditions for the desired products with a fair degree of accuracy on the basis of the physical characteristics of the charging stock.

In making a run the preliminary operations include: 1, heating the lead up to the operating temperature; 2, evacuating the system to 29 inches of mercury or less; 3, cooling the water supply to the jet condenser and regulating the water flow to balance the circulating pump; and, 4, weighing the charge into the feed tank and pre-heating it to 250°F. With the above adjustments complete, steam is admitted into the vaporizer and regulated—the flow being indicated by an orifice meter. Ordinarily, from one to three pounds of steam per gallon of charge are used. The needle valve in the charging line then is opened to give a charging rate of approximately four liters per hour. The charging rate then is checked by observing the rate of fall of the liquid level in the feed tank gage glass. Likewise, the distillate rate is checked by observing the rise of the liquid level in the distillate-receiver gage glass.

At the end of each run the pre-heater coil is blown free of oil by admitting steam just ahead of the charging valve. This prevents coking in the coil. Any light distillate which gets past the distillate spray trap is recovered by draining the water from the cooling system and separating the oil.

TABLE 3
Flash Vacuum Distillation of Butler County, Kansas, Residuum

	Charging Stock	Run No. 1	Run No. 2	Run No. 3
Operating Data:				
Lead-bath temperature, °F	.....	700	750	800
Vapor temperature, °F	.....	525	637	700
Steam ratio, pounds of water per gallon of distillate	.....	3.75	2.99	4.12
Yield of distillate, percent	.....	68.1	83.3	91.5
Yield of tar, percent	.....	30.7	15.6	7.7
Loss, percent	.....	1.2	1.1	0.8
Quality of Products:				
Distillate				
Color, iodine	37,800	512	880	3,300
*Color removed, percent	.....	90.8	98.1	92.0
Gravity, deg. API	23.8	27.0	26.4	25.0
Viscosity, Saybolt Universal at 210 deg. F., sec	52	39	41	45
Tar				
Gravity, deg. API	.....	15.1	13.0	....
Softening point, °F	....	72	144	426

*Percent color removed = 100 − (Iodine color of distillate × yield of distillate) / Iodine color of charge

TABLE 4
Flash Vacuum Distillation of Oklahoma City Residuum

	Charging Stock	Run No. 19	Run No. 18	Run No. 17
Operating Data:				
Lead-bath temperature, °F	....	740	775	820
Vapor temperature, °F	....	630	658	715
Steam ratio, pounds of water per gallon of distillate	....	3.98	3.68	3.75
Yield of distillate, percent	....	87.0	90.5	94.6
Yield of tar, percent	....	11.5	8.3	5.2
Loss, percent	....	1.5	1.2	0.2
Quality of Products:				
Distillate				
Color, iodine	12,600	758	820	1,610
Color removed, percent	....	94.7	94.1	87.9
Gravity, deg. API	25.9	27.6	27.3	27.0
Viscosity, Saybolt Universal at 210 °F., sec	57	48	49	50
Tar				
Softening point, °F	....	75	85.5	105

An example of the flexibility of the vacuum-flash unit is afforded by a comparison of three runs made on a sample of long residuum from Butler County, Kansas, crude oil. Operating data and the characteristics of the products are shown in Table 3.

It can be seen from the percent of color removed from the distillate that the unit is efficient for de-asphaltizing long residuum. Wide variations in the properties of the tar result from relatively small changes in operating temperature with this particular charging stock, which is decidedly asphaltic in nature.

Results of a similar series of runs on a long residuum from Oklahoma City crude oil are shown in Table 4.

The softening point of the tar is considerably less affected by the flash temperature in the case of this charging stock, which is representative of the Mid-Continent type. Color-removing efficiency remains in the same range.

The unit is capable of handling a large variety of products. On one occasion pressure fuel oil was distilled without difficulty. No appreciable coking occurs in the pre-heater coil or the vaporizer under ordinary operating conditions, and the only time any difficulty has been encountered was during an attempted run at 1000°F.—when the tar produced (due to its high melting point) failed to flow down into the residuum receiver, and coking of the evaporator resulted.

Flash distillation without steam may also be accomplished. For this purpose the unit is operated at 5 mm., or less, absolute pressure; and the steam condenser is employed to insure complete condensation of the lighter fractions. Somewhat lower charging rates are necessary to obtain adequate stripping of the tar.

FRACTIONATION OF FLASH VACUUM DISTILLATE

The fourth distilling unit of this group was designed to reduce the flash vacuum distillate to cylinder-stock viscosity and fractionate the overhead products. This unit is of the batch type, and was designed to operate under either dry vacuum at pressures down to 2 mm., absolute, or wet vacuum at somewhat higher pressures.

As shown in Figure 4, the unit consists of a horizontal, cylindrical still equipped with a fractionating column, a partial condenser for controlling reflux, a condenser and cooler, and distillate receivers for collecting and removing overhead fractions. The still

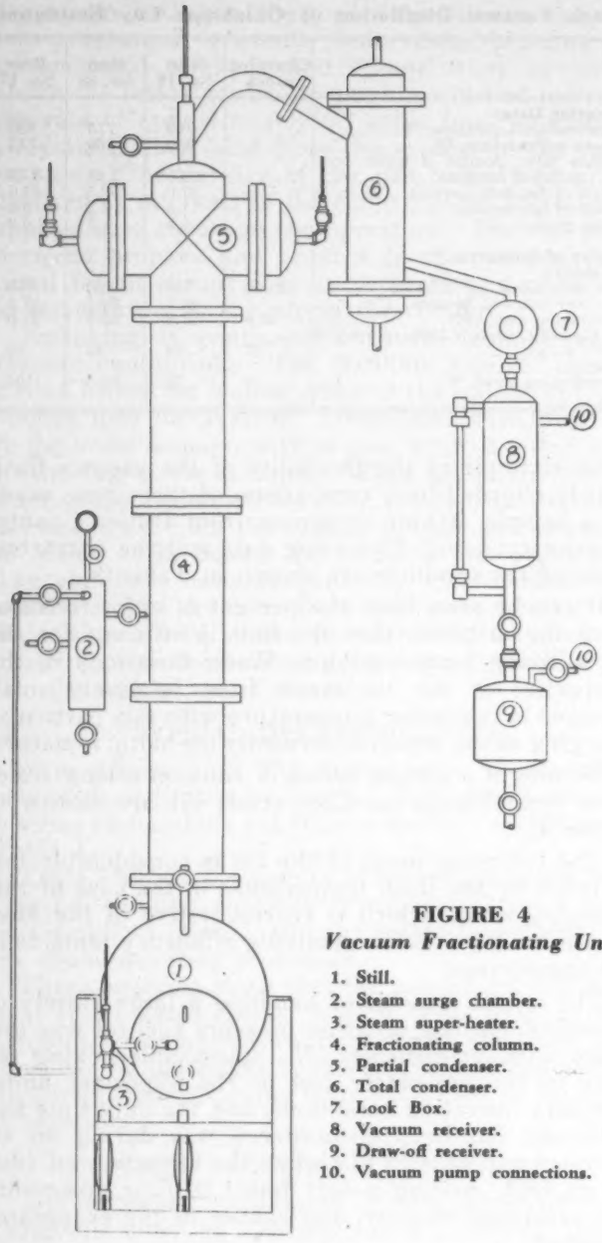

FIGURE 4
Vacuum Fractionating Unit

1. Still.
2. Steam surge chamber.
3. Steam super-heater.
4. Fractionating column.
5. Partial condenser.
6. Total condenser.
7. Look Box.
8. Vacuum receiver.
9. Draw-off receiver.
10. Vacuum pump connections.

has a charging capacity of approximately three gallons; and is provided with an open steam coil in the bottom, through which super-heated steam may be admitted.

The fractionating column is built in three sections, each section being 12 inches long and four inches in diameter. A perforated plate in the bottom of each section serves as a packing support, and also re-distributes the reflux. This obviates the possibility of channeling through the entire length of packing. The sections are packed with wire coils. These coils were made by winding 16-gage galvanized wire around a ¼-inch diameter rod, then cutting the coil into ⅜-inch lengths.

The use of a partial condenser was considered the simplest method of controlling reflux in this type of unit. In this case the partial condenser is built into the top section of the column. Seven horizontal tubes spaced in three rows extend through the column, and are welded to header plates on each side. Provision is made for cooling, either with water from a constant-head device or with a stream of air metered through an orifice. The approximate volume of reflux can be calculated from inlet and outlet temperatures of the cooling medium and the volume of flow.

The top of the still, fractionating column, and partial condenser are completely insulated with 3½ inches of 85 percent magnesia pipe covering.

Distillation rate is observed through a look box in the distillate line and by the rise of the liquid level in the calibrated gage glass of the first receiver. An auxiliary pump is required to evacuate the lower receiver, which is used to remove fractions from the system. A mercury-column regulator is provided for regulating the system pressure at any desired point between 2 mm. and 25 mm., absolute. A McLeod gage (0.25 mm.) is connected through a manifold to the still, the top of the fractionating column, and the distillate receiver so that pressures may be checked at these three points.

The actual operation of this distilling unit depends largely upon the nature of the charge being distilled, particularly with regard to the vacuum employed and whether or not steam is used. Generally, flash vacuum distillates of the Mid-Continent type may be reduced to 100 to 120 viscosity at 210°F. with dry vacuum

(Continued on page 306)

TABLE 5
Comparison of Properties of Fractions from Laboratory Unit with Those of Components of Blend Charged

	Gas Oil		Light Wax Distillates			Heavy Wax Distillate		Overhead Cylinder Stock	
	Commercial Unit	Laboratory Unit	Commercial Unit	Laboratory Unit		Commercial Unit	Laboratory Unit	Commercial Unit	Laboratory Unit
				1	2				
Distillation:				Deg. F.					
Initial boiling point	432	490	634	648	723	804	793	831	924
5 percent point	525	527	668	662	761	859	826	924	955
10 percent point	546	555	686	667	768	876	836	943	960
20 percent point	575	580	707	675	775	886	847	966	970
30 percent point	589	591	726	680	778	894	855	981	984
40 percent point	596	597	743	683	781	900	866	999	1,000
50 percent point	610	606	760	690	788	907	871	1,014	1,014
60 percent point	618	613	777	698	795	917	881	1,035	1,036
70 percent point	630	620	791	704	800	928	890	1,054	1 054
80 percent point	645	630	807	711	807	948	902	1,075	1,078
90 percent po nt	667	641	826	725	819	979	922	1,093	1,095
95 percent point	706	653	840	735	829	1,006	940	....	....
End point	800*	669*	860*	745*	838*	1,056*	970*	1,113*	1,115*
Average boiling point	611	590	756	666	788	917	876	1,000	1,020
Boiling range	368	179	226	97	115	252	177	282	191
Gravity, deg. API	34.5	34.3	30.1	31.3	28.5	24.7	24.2	21.5	21.4
Yield, percent	....	15.8	....	21.4	23.0	....	16.8	....	23.0
Blend, percent	15.9	....	44.2	....	....	17.6	....	22.3	....

*Extrapolated. Distillations made at 2 mm., absolute, pressure and values converted to 760 mm.

Recent Developments

In Selective Solvent Extraction With Chlorex

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THIS paper discusses developments in the Chlorex process during the past year. Seven Chlorex plants are now in operation. Four of these plants are in the Pennsylvania region. Descriptions of these plants and typical results secured by Chlorex extraction of overhead and residual lubricating stocks from Pennsylvania crude are given. Chlorex is also well suited to the treatment of overhead stocks from Mid-Continent and Coastal crudes. Typical results on such stocks are included in the paper. The possibilities of blending a 100- to 105-VI Chlorex-treated Mid-Continent neutral with, 1, conventionally-refined 150-viscosity Mid-Continent bright stock of 80-85 VI and, 2, the same Mid-Continent bright stock, which has been Chlorex-treated with a small extract loss, are illustrated by the inspections of two series of motor oil blends—SAE 20 to SAE 50, inclusive, made up by blending the Chlorex-treated neutral with the two bright stocks mentioned above. Properties of the blended oils are discussed, with particular regard to the viscosity index, carbon residue, and oxidation resistance of the oils of both series. Results secured by Chlorex extraction of a Mid-Continent long residuum after preliminary asphalting in propane solution, or acid-treating, are also included.

This paper was presented at Fifth Mid-Year meeting, American Petroleum Institute, Tulsa, May 16, 1935.

THE Chlorex process of selective solvent extraction was brought to the commercial stage by Mid-Continent Petroleum Corporation and Standard Oil Company (Indiana)—both companies acting independently and without knowledge of the other's development. Carbide and Carbon Chemicals Corporation, sole manufacturers of Chlorex* (β, β' dichlorethyl ether) has received an exclusive license under an agreement with Mid-Continent and Standard to sell Chlorex to other refiners as a selective solvent in refining lubricating oils. Those refiners who purchase Chlorex from Carbide and Carbon Chemical Corporation receive protection under the patent rights of Mid-Continent and Standard. Chlorex is manufactured by processes developed by the Carbide and Carbon Chemicals Corporation, which processes are covered by its issued patents and pending applications. The present market price for Chlorex in tank cars is 14½ cents per pound, f.o.b. the producing plant at South Charleston, W. Va. This is all the refiner is required to pay. There is no royalty charge based on plant capacity.

There are now seven commercial Chlorex plants operating, with a combined charging capacity in excess of 6000 barrels of oil per day. Below is a list of these plants with the daily charging capacity of each. The Freedom and Bradford Penn installations recently were placed in operation. The other five have been running for some time, and have treated a total of something like 60,000,000 gallons of oil.

Plant	Daily Oil-charging Capacity (42-Gallon Barrels)
Standard Oil Co., (Indiana), Casper, Wyo.	600
Standard Oil Co., (Indiana), Wood River, Ill.	1,000
Mid-Continent Petroleum Corp, Tulsa., Okla.	200
The Pennzoil Co., Oil City, Pa.	1,000
Socony-Vacuum Oil Co., Inc., Olean, N. Y.	1,700
Freedom Oil Works Co., Freedom, Pa.	1,200
Bradford Penn Refining Corp., Clarendon, Pa.	450
Total	6,150

The plant operated by Standard Oil Company at Casper, Wyoming, is treating overhead stocks from Salt Creek crude. The units at Wood River, Illinois, and Tulsa, Oklahoma, are treating oils from Mid-Continent crude. The other four plants were installed during the past 12 months for refining Pennsylvania oils.

DEVELOPMENTS IN PENNSYLVANIA REGION

The Pennzoil Company placed its Chlorex plant in operation last June. This plant has treated neutrals, bright stock, and 600-flash steam-refined cylinder stock with uniformly good results. In the treatment of cylinder stock and neutrals by The Pennzoil Company, raffinate yields of 90 to 92 percent, or better, have been secured. They have enjoyed a very considerable improvement in filter yields when finishing cylinder-stock raffinates to bright stock color specifications. No difficulties have been encountered in dewaxing the wax-bearing raffinate; in fact, they have removed a drier petrolatum stock in the plant centrifuges, using the same chilling temperature and naphtha dilution as formerly on filtered cylinder stock. It is necessary to use a slightly higher water temperature on the centrifuge bowls to facilitate removal of the higher-melting-point wax.

The extraction equipment at Pennzoil is a three-

*Trademark registered U. S. Patent Office.

TABLE 1
Data on Pennsylvania Neutral

	Original	Raffinate	Extract
Yield, percent by volume	100.0	92.1	7.9
Gravity, API	30.1	31.5	15.3
Flash point, °F.	425	425	...
Fire point, °F.	500	500	...
Pour point, °F.	20	25	...
Color, NPA	3.5	2.5	...
Carbon residue, percent	0.03	0.01	...
Sligh oxidation No.	28.4	3.4	...
Saybolt Universal viscosity at 100 °F.	179	168	927
Saybolt Universal viscosity at 210 °F.	45.8	45.6	62.5
Viscosity index	109.1	117.5	—12.1

stage counter-current system of mixers and settlers. Mixing is accomplished by orifice-plate pipe mixers. These have proved very efficient as a means of contacting the solvent and oil. Chlorex now is recovered from the extract and raffinate solutions in a pipe still incorporating a vacuum stripper.

The Chlorex plant operated by Socony-Vacuum Oil Company, Inc., at Olean, N. Y., has a charging capacity of 1700 barrels per day. This unit has operated continuously since early last August. The extraction equipment consists of a four-stage counter-current system of settling tanks and mixers. Chlorex is recovered from the raffinate and extract solutions in shell stills which are designed for, and maintained under, a vacuum of 26 inch mercury. Heat for distillation is supplied with closed steam coils using 140 pounds live steam. Each still is also provided with open steam coils to facilitate the stripping operation. Two 400 barrel stills are used for recovering the solvent from the raffinate solution, and four of the same capacity for the extract solution.

In both the Pennzoil and Socony-Vacuum plants considerable equipment which was available in the refinery, including the distillation equipment in both cases, was utilized in construction. The installations for the Freedom Oil Works Company and the Bradford Penn Refining Corporation are new from the ground up.

The Freedom unit has a charging capacity of 500 barrels per day of 600 steam-refined cylinder stock or up to 1200 barrels per day of neutral. The solvent is recovered from the extract and raffinate solutions continuously in separate steam-heated stripping columns maintained under a vacuum of 28 inch mercury. Complete removal of the solvent is effected at a maximum stripping temperature of 300°F. In the Bradford Penn Chlorex plant, heat for distillation under a vacuum at 26-28 inch mercury is applied by means of a hot oil circulating system. The Bradford Penn plant has a capacity of 300 barrels per day of cylinder stock or 450 barrels of neutral.

RESULTS SECURED WITH CHLOREX ON PENNSYLVANIA STOCKS

Typical results on a 180 neutral from Pennsylvania crude are shown in Table 1. This distillate was treated with Chlorex in seven-stage continuous counter-current apparatus with a ½-to-1 ratio of Chlorex to oil by volume at a temperature of 65°F.

A 92.1 percent yield of oil was obtained, which shows an improvement in viscosity index from 109.1 to 117.5. Increased oxidation resistance is indicated by the reduction in Sligh No., although some feel that this test is more qualitative than quantitative. The laboratory where this extraction was conducted is not yet equipped to run the Indiana oxidation test, which many consider gives a better index of oxidation resistance of an oil than the Sligh test does. The viscosity index of this neutral was increased to 121.2 in another extraction, using the same number of counter-current stages, a higher Chlorex-to-oil ratio (1 to 1), and a higher temperature, 80°F. Under these conditions, improvement in the oxidation resistance, as measured by the Sligh No., was the same. Raffinate yield was slightly lower.

In considering solvent extraction as applied to Pennsylvania oils, refiners in that region are interested principally in the treatment of steam-refined cylinder stock. By four-stage counter-current treatment of a typical 600 stock, results shown in Table 2 were obtained. The oil was treated at a temperature of 75°F. using a 1.5-to-1 Chlorex-to-oil ratio, by volume.

It will be noted that the extract loss on this stock was only seven percent. The extract has a gravity of 10.9 (nearly the same as that of water) a viscosity of 1445 sec. at 210°F., and a viscosity index of approximately —30. The character of this extract clearly demonstrates the high selectivity of the solvent. By treating this stock with Chlorex, a 93.0 percent yield of wax-bearing raffinate was obtained, with a reduction in the Conradson carbon residue from 2.07 percent to 1.40 percent. When the original stock and raffinate were dewaxed to pour points of +25 and +20°F., respectively, and both oils were filtered to an 8 NPA color, it will be noted that the treated bright stock had a carbon residue of 0.91 percent as compared with 1.44 percent on the conventionally-refined bright stock. At the same time, the percolation yield was increased from 446 gallons

TABLE 2
Data on Pennsylvania Steam-Refined Cylinder Stock

	Original Charging Stock			Raffinate			Extract from Original
	Wax-bearing	Dewaxed	Finished	Wax-bearing	Dewaxed	Finished	
Yield, percent by volume	100	...	...	93.0	...	...	7.0
Gravity, API	26.9	26.6	27.2	28.1	27.8	28.2	10.9
Flash point, °F.	590	585	585	585	580	580	...
Pour point, °F.	50	30	25	55	25	20	...
Carbon residue, percent	2.07	1.90	1.44	1.40	1.33	0.91	...
Color, true	1,500	1,700	333	1,100	1,190	260	...
Color, NPA	...	...	8	...	...	8	...
Acidity	0.56	0.12	0.10	0.39	0.07	0.06	...
*Viscosity at 210 °F.	161.2	173	159.9	150.9	161.8	152.4	1,445
*Viscosity at 130 °F.	887	...	...	784	...	...	...
*Viscosity at 100 °F.	2,231	2,695	2,338	1,908	2,272	2,083	...
Viscosity index	109	104.5	105.5	112.0	108.3	108.5	—30 approximate
Viscosity-gravity constant	0.804	0.805	0.802	0.796	0.797	0.795	0.907

*Kinematic viscosity converted to Saybolt seconds by means of A. S. T. M. equations.

TABLE 3
Percolation Yields

STOCK	Color (NPA)	Percolation Yield (Gallons of Viscous Oil Per Ton of No. 1 Attapulgus Clay)
Original	6	376
	7	392
	8	446
Raffinate	6	467
	7	490
	8	562

per ton to 562 gallons per ton, which represents a considerable saving in filter costs for the same bright stock color. A comparison of the percolation yields when finishing the dewaxed charging stock and the dewaxed raffinate to various NPA colors will be found in Table 3.

The increased demand for lighter lubricating oils has placed a premium on neutrals. Pennsylvania neutrals are selling for around 28 cents a gallon, while the price of bright stock has dropped to around 16 cents a gallon. This situation is just about the average of what it was a year or so ago. When treating a Pennsylvania steam-refined cylinder stock with Chlorex, a reduction in the viscosity at 210°F. of from 10 to 12 seconds is obtained. This offers two advantages: 1, Starting with a 600-flash cylinder stock with a viscosity of 150 seconds at 210 °F., Chlorex treatment makes it possible to finish up a less viscous (140-138 seconds at 219°F.) bright stock. By this reduction in viscosity about three percent to four percent more bright stock will go into motor oil blends than when refining conventionally by dewaxing and percolating to the same pour point and color; because without the solvent the reduction in viscosity at 210°F. is very slight. 2, Starting with a cylinder stock of 160-162 seconds at 210°F., Chlorex extraction by reducing the viscosity will permit finishing up a bright stock of 150-148 at 210°F. When running to the more viscous cylinder stock, some of the viscous oil which normally goes into the bright stock is taken into a slop wax cut, which may be dewaxed with propane or thermally-treated to permit filter pressing for wax removal. It has been estimated by several Pennsylvania refiners that, taking all factors into consideration, the latter method described above will show an increase in neutral production of 2 to 2½ percent, based on the crude, or 17 to 20 percent, based on neutral, and a decrease in bright stock production of about 2½ to 3 percent based on the crudes, or 15 to 20 percent based on bright stock.

Many Pennsylvania refiners feel that viscosity reduction of cylinder stocks by solvent means will pay for the cost of extraction and also compensate for extract losses which are sustained in solvent treating. Considering this, and the increase in percolation yields obtained, Chlorex extraction of Pennsylvania oils should not increase refining costs, and may show some savings. Profitable disposal of extracts is being closely studied, and applications in certain directions offer promise.

With regard to improvement in oxidation resistance, conventionally-refined Pennsylvania SAE-20 and -30 motor oils will generally show about 50 to 55 hours for 10 mg. of sludge on the Indiana oxidation test. A number of oxidation tests have been run on SAE-20 and -30 blends made up of Chlorex-treated neutral and bright stock. All of these have shown better than 200 hours on the Indiana test with no sludge formation.

TREATMENT OF LUBRICATING STOCKS FROM MID-CONTINENT AND COASTAL CRUDES WITH CHLOREX

Chlorex is peculiarly well suited to the treatment of overhead stocks from Mid-Continent and Coastal crudes. Results obtained with Chlorex on a typical SAE-20 Mid-Continent distillate, dewaxed to a 25°F. pour point, are shown in Table 4. This oil was treated in six-stage, continuous, counter-current extraction equipment at a temperature of 60°F., using a 1.44-to-1 Chlorex-to-oil ratio.

TABLE 4
Data on Mid-Continent Distillate

	Original	Raffinate
Yield, percent by volume	100	71.5
Gravity, API	24.0	30.0
Saybolt Universal viscosity at 210 °F	52.7	49.9
Saybolt Universal viscosity at 100 °F	348.1	267.8
Viscosity index	60.5	92.5
Viscosity-gravity constant	0.853	0.815
Color, NPA	....	4½ to 5
Color, true	331	50
Pour point, °F.	25	30
Carbon residue, percent	0.17	0.02
Emulsion test in 1 hour	2 cc.	OK
Neutralization No	0.36	0.14

A very marked improvement in the color has been effected by the action of Chlorex alone. The stock came direct from the still, and received no acid or clay treatment prior to Chlorex extraction. A 71.5 percent yield of raffinate was obtained, showing an improvement in viscosity index from 60.5 to 92.5 With a 63 percent yield, a viscosity index of 100 was readily obtained on this oil.

The raffinate was finished to a 3½-4 color with a clay yield of 4000 gallons per ton of No. 1 Attapulgus clay.

When treating distillates from Coastal crudes, low yields must be expected if a 100-VI oil is desired. For this reason, a moderate improvement in viscosity index appears more logical. Table 5 shows results obtained with Chlorex on overhead distillate blend from Coastal crude. This extraction was run seven-stage, batch, counter-current, at a temperature of 60°F. using a 1½-to-1 Chlorex-to-oil ratio.

With a 64.8 percent raffinate yield a viscosity-index improvement from 21 on the original stock to 65.5 on the raffinate was obtained. The raffinate was finished to a 2½ NPA color, with a percolation yield of 5900 gallons per ton of No. 1 Attapulgus clay. Chlorex extraction of this stock is accompanied by improvement in other properties, such as steam-emulsion number, demulsibility, and acidity.

Several of the refiners in the Mid-Continent field are considering installation of a Chlorex plant to treat Mid-Continent neutrals and possibly bright stock. On a Mid-Continent neutral, a viscosity index of 100, or better, can be obtained readily with Chlorex, with yields from 60 percent to 75 percent. Acid treatment will not be necessary, and solvent treatment should show real savings in clay costs. Assuming that such a neutral were available, motor oil blends could be made with this neutral and: *1*, 150-viscosity Mid-Continent bright stock finished

TABLE 5
Data on Distillate Blend from Coastal Crude

	Original	Raffinate Before Claying	Raffinate Finished	Extract
Yield, percent by volume	100	64.8	...	35.2
Gravity, API	20.4	25.0	25.0	11.9
Color, true	85	34	7	...
Color, NPA	...	4½	2½	...
Pour point, °F	—10	—5	0	...
Carbon residue, percent	0.16	0.02	0.01	...
Saybolt Univ. vis. at 210 °F	61	59.9	60.2	93.8
Saybolt Univ. vis. at 100 °F	741	544	550	...
Viscosity index	21	65.5	67	...
Viscosity-gravity constant	0.875	0.840	0.839	0.937

conventionally with acid and clay or, *2*, the same bright stock which has been treated with Chlorex with a moderate extract loss of, say, 12½ percent.

In order to study these possibilities, two series of motor oil blends, SAE-20 to SAE-50, inclusive, have been prepared. The same neutral, a typical Chlorex-treated Mid-Continent distillate of 102 VI was used in both series. Tests of this neutral and the Chlorex-treated and untreated bright stocks are given in Table 6.

The data in Table 6 show that Chlorex treatment of the conventionally refined Mid-Continent bright stock has resulted in a reduction in Conradson carbon residue from 1.79 to 1.11 percent on the treated oil. There is no increase in pour point. The viscosity index has been increased from 80 to 89.

Inspections on motor-oil blends, secured by blending the Chlorex-treated neutral with the conventionally refined Mid-Continent bright stock, are given in Table 7.

The viscosity index of the SAE-20 oil in Table 7 is better than 100, while the viscosity index of the SAE-30 oil is slightly under 100. There is a progressive improvement in the oxidation resistance of these oils, as measured by the Sligh test, which is to be expected as the amount of bright stock in each blend increases.

The viscosity indices in Table 7 were calculated from the Saybolt Universal viscosities of these oils. If these figures had been based on the kinematic viscosities, it is probable that the viscosity indices would have been somewhat lower. Although many feel that viscosimeters for measuring kinematic viscosities give more accurate results than the Saybolt instrument, particularly on the lighter oils, it is, nevertheless, true that the Saybolt viscosimeter is in very general use throughout the country, and Saybolt viscosities are still used generally in reporting

TABLE 6
Data on Mid-Continent Neutral and Bright Stocks

	*Neutral	Bright Stock	Treated Bright Stock (87.5-Percent Yield)
Gravity, API	31.1	23.2	25.4
Flash point, °F	430	555	560
Fire point, °F	490	635	640
Pour point, °F	5	5	5
Color, Tag-Robinson	...	1	1
Color, NPA	2½	...	...
Color, ASTM	2—	4— dilute	4— dilute
Carbon residue, percent	0.018	1.79	1.11
Saybolt Univ. vis. at 100 °F	211	3,512	2,609
Saybolt Univ. vis. at 130 °F	110†	...	...
Saybolt Univ. vis. at 210 °F	47.5	162.5	145.9
Viscosity index	102	80	89

*Contains 0.1 percent paraflow.
†A.S.T.M. chart.

oil specifications. Further improvement in the viscosity index of the oils in Table 7 can be secured by the addition of Paratone to the bright stock used in the blends.

Inspections on a series of motor oils made by blending Chlorex-treated Mid-Continent neutral with the 150 bright stock after treatment with Chlorex, with a 12½ percent loss, are shown in Table 8.

It will be noted that the SAE-20 and SAE-30 oils both have a viscosity index of better than 100, while the SAE-40 oil has the same viscosity index as the SAE-30 oil in Table 7. As a result of the increased demand for lighter oils, it appears that the bulk of the demand for motor oils will be supplied with

TABLE 7
Blend of Chlorex-treated Neutral and Conventionally-Refined Bright Stock

	SAE-20	SAE-30	SAE-40	SAE-50
Neutral, percent by volume	93	73	59	43
Gravity, API	30.4	28.9	27.9	26.6
Flash point, °F	435	455	465	475
Fire point, °F	500	515	525	540
Pour point, °F	5	5	5	5
Color, ASTM	3.5	5—	6—	6
Carbon residue, percent	0.10	0.42	0.74	1.0
Saybolt Univ. vis. at 100 °F	248	405	593	914
Saybolt Univ. vis. at 130 °F	129	196	269	370*
Saybolt Univ. vis. at 210 °F	49.6	58.3	67.4	81.0
Viscosity index	101	97	93	88
Sligh No.	2.7	2.5	1.5	1.0

*From A.S.T.M. chart.

SAE-30 grade, or lighter. Table 8 shows that oils of 100 viscosity index, or better, to meet this demand can be made by blending a Chlorex-treated Mid-Continent neutral with a conventionally refined Mid-Continent bright stock, also treated with Chlorex with a low extract loss.

TABLE 8
Blends of Chlorex-treated Neutral and Bright Stocks

	SAE-20	SAE-30	SAE-40	SAE-50
Neutral, percent by volume	93	71	54	40
Gravity, API	30.7	29.4	28.5	27.7
Flash point, °F	435	455	465	475
Fire point, °F	500	515	525	540
Pour point, °F	5	5	5	5
Color, ASTM	3.5	5—	6—	6
Carbon residue, percent	0.07	0.28	0.42	0.56
Saybolt Univ. vis. at 100 °F	244	394	594	849
Saybolt Univ. vis. at 130 °F	129	194	271	355*
Saybolt Univ. vis. at 210 °F	49.5	58.5	68.5	80.9
Viscosity index	102	102	97	95
Sligh No.	1.5	1.3	0.6	0.6

*From A.S.T.M. chart.

Also of interest is the improvement in Conradson carbon residue which has been obtained by blending the neutral with the Chlorex-treated rather than the conventionally refined bright stock. The carbon residues in Table 8 are approximately half those in Table 7. Further improvement in resistance to oxidation, as measured by the Sligh No., has been obtained by treating both blending stocks with Chlorex.

TREATMENT OF MID-CONTINENT LONG RESIDUUM WITH CHLOREX

Although Chlorex shows a very marked improvement, with low extract losses, on residual stocks from Pennsylvania crude, when extracting a Mid-Continent long residuum, which may contain from 5 to 15 percent asphalt and other undesirable constituents, it is usually necessary to acid-treat the

TABLE 9
Data on Oklahoma City Long Residuum

	Original Wax-bearing Stock	Original Stock De-asphalted (Dewaxed Only)	Raffinate from De-asphalted and Dewaxed Stock	Finished Raffinate*	Extract from De-asphalted and Dewaxed Stock
Yield, percent by volume	100	76.2	58.0	98	42
Overall yield, percent	100	76.2	44.2	43.6	...
Gravity, ° API	19.9	20.7	26.3	27.7	11.8
Saybolt Universal viscosity at 210° F.	141	128.5	113.6	92.2	235
Saybolt Universal viscosity at 100° F.	3,180	2,709	1,581	1,050	...
Viscosity index	68.5	65.5	94.6	98.4	—78 approx.
Viscosity-gravity constant	0.861	0.856	0.816	0.809	0.922
Color, true	10,100	2,000	1,650	25	...
Color, NPA	...	...	...	3½ to 4	...
Pour point, ° F.	75	0	5	5	...
Neutralization No.	0.16	0.15	0.15	0.14	...
Carbon residue, percent	5.93	3.22	1.53	0.34	...

* Raffinate percolated through No. 1 Attapulgus clay.

stock or de-asphalt it in propane before solvent extraction. Typical results obtained on a propane-de-asphalted Oklahoma City long residuum with Chlorex are given in Table 9. The de-asphalted stock was treated in seven-stage, batch, counter-current equipment at a temperature of 80°F. with a 2-to-1 Chlorex-to-oil ratio by volume.

This same stock was extracted with Chlorex after acid treating with one pound of acid per gallon, under the following conditions:

Chlorex-to-oil ratio .....2 to 1
Extraction temperature .....100°F.
Method—four-stage, batch, counter-current

The yields secured are given in Table 10, and it will be noted that there is some sacrifice in yield when using acid instead of propane for de-asphalting—although the physical properties of the finished oil were equally good. In acid treating, however, no additional investment is required for equipment, as the present acid treating plant may be used for this preliminary step—thus eliminating the investment required for a propane de-asphalting plant.

As a matter of interest, a Mid-Continent long residuum, conventionally refined by acid treatment, by centrifugal dewaxing, and by percolation, was treated in seven-stage continuous, counter-current apparatus at a temperature of 105°F., using a 3-to-1 Chlorex-to-oil ratio. The results are given in Table 11.

A 72.4 percent yield of 99.2-VI oil was secured. This extraction was run simply to determine what loss would be encountered in making a 100-VI oil from an 80- to 85-VI conventionally refined Mid-Continent stock of this kind. By the use of a vacuum still, those refiners who are running a long residuum can take their lubricating stocks overhead from the topped crude. This method of refining will provide greater flexibility in controlling neutral and bright stock production to meet changing marketing conditions, and the overhead stocks will be clean and relatively free from asphaltic materials—and may be readily solvent-extracted with a single solvent, such as Chlorex. The Chlorex process may be installed and operated at surprisingly low cost.

TABLE 10
Data on Oklahoma City Long Residuum

	Original Wax-bearing Stock	Original Wax-bearing Stock Acid-treated	Raffinate from Acid-treated Stock	Dewaxed Raffinate	*Percolated Dewaxed Raffinate
Yield, percent by volume	100	69.2	65.7	75	95
Over-all yield, percent	100	69.2	46.4	34.8	33.0

*Percolated to 4-4½ NPA color.

TABLE 11
Data on Mid-Continent Long Residuum

	Original Oil	Raffinate	Contacted Raffinate	Extract
Contact clay, gallons per ton	...	...	8,000	...
Yield, percent by volume	100	72.4	...	27.6
Gravity, API	25.0	28.4	28.5	16.7
Viscosity-gravity constant	0.828	0.802	0.802	0.893
Flash point, °F.	470	480	480	460
Fire point, °F.	545	560	560	530
Pour point, °F.	5	5	5	10
Color, Tag-Robinson	1¾	1¼	1¼	¼
Carbon residue, percent	1.15	0.59	0.57	2.80
Saybolt Univ. vis. at 100 °F.	1,237	1,103	1,112	2,792
Saybolt Univ. vis. at 210 °F.	91.6	94.8	95.2	105.7
Viscosity index	81.9	98.7	99.2	10.8

CHLOREX PLANT INSTALLATION AND OPERATING COSTS

Figure 1 is a typical flow diagram of a Chlorex plant using the latest design of extraction equipment and vacuum distillation for continuous recovery of the solvent from the raffinate and extract solutions. Operation is as follows:

The charge oil is pumped through a heat exchanger **M**, which is operated either as a cooler or heater, depending on whether water or steam is circulated through the unit. Chlorex-extraction temperatures range from 60 to 125°F., depending on the stock and the results desired. The rate of pumping of the

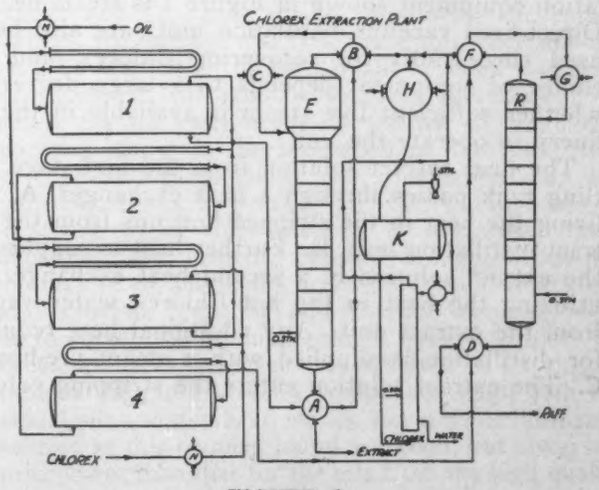

FIGURE 1

charge oil is under automatic flow control. The pre-heated or pre-cooled oil is mixed in the first-stage pipe mixer, with the extract solution (thrice-used Chlorex) from the second stage. This mixture then settles in the first-stage settling tank. The extract solution from the first-stage settler is pumped, under automatic float control, to the extract-solution distillation unit for continuous recovery of the solvent. The raffinate solution from the first stage flows under first-stage pressure, and is mixed in the second-stage pipe mixer with the extract solution from the third stage. This mixture settles in the second-stage settling tank. The raffinate solution from the second-stage settler is mixed with the extract solution from the fourth stage (once-used Chlorex) in the third-stage pipe mixer, and this mixture settles in the third-stage settling tank. The raffinate solution from the third-stage settling tank is mixed with fresh Chlorex in the fourth-stage pipe mixer. This mixture settles in the fourth-stage settling tank. The final raffinate solution, from the fourth stage, is pumped under automatic control to the raffinate-solution distillation unit for continuous recovery of the solvent.

Figure 1 illustrates a design for four-stage counter-current operation. There does not appear to be any advantage in going to more stages when treating overhead or residual stocks from Pennsylvania crude. However, when treating Mid-Continent and Coastal oils, it is usually desirable to use 5, 6, or even 7 stages. When using more stages, the operation of the extraction equipment is the same as described above.

A compact extraction unit is made by installing the horizontal settling tanks one above the other in structural-steel framework. The first (top) stage is maintained under the highest pressure, varying from 75 to 100 pounds per square inch. The pressure drops in increments of 10 to 15 pounds per stage as the raffinate solutions flow downward from stage to stage, while the extract solutions are pumped with float-controlled pumps in the opposite direction. Chlorex is charged to the system with an automatically-controlled pump through a heat exchanger, **N**, through which either water or steam may be circulated for heating or cooling the solvent.

The solvent-recovery system is maintained under a vacuum of 26 to 28 inch mercury, and the solvent is completely recovered from the oil at a maximum stripping temperature of 300 to 325°F. The distillation equipment shown in Figure 1 is steam-heated. Direct-fired vacuum distillation units are also being used successfully for recovering Chlorex, and the choice of equipment depends to a large degree on whether sufficient live steam is available in the refinery to operate the unit.

The final extract solution from the first-stage settling tank passes through a heat exchanger, **A**, utilizing the heat in the stripped bottoms from the extract distillation unit, **E**. Further heat is supplied to the extract solution in a second heat exchanger, **B**, utilizing the heat in the hot Chlorex water vapors from the extract unit. Any additional heat required for distillation is supplied with a steam pre-heater, **C**. The extract solution enters the stripping column near the top. Open steam is applied at the bottom of the column. Re-boiler coils may be used to maintain the temperature throughout the column, which is a simple fractionating column with bubble trays.

The final raffinate solution from the fourth stage is heated with bottoms and vapor heat exchangers, **D** and **F**, and a steam pre-heater, **G**. As the raffinate solution will contain only 15 to 25 percent solvent, the raffinate stripping unit, **R**, is considerably smaller than the extract unit, **E**, where the bulk of the solvent is recovered. Hot Chlorex water vapors from the extract and raffinate solution distillation units pass through a water-cooled condenser, **H**—the condensed Chlorex and water flowing to a settling tank, **K**, where the solvent is separated from the water by gravity and returned to storage for re-use. The water will be saturated with Chlorex with a solvent content of approximately one percent. This water is fed through a pre-heater to a small, packed column, which may be readily constructed from a piece of casing of the proper length and diameter. Open steam is added near the bottom of this column. Water which is completely denuded of Chlorex flows to the sewer under automatic float control from the bottom of this tower, while the vapors which are rich in Chlorex pass to the raffinate extract vapor condenser, **H**. A vacuum is maintained on the system by means of a steam-jet vacuum pump. It is not necessary to operate the water-stripping column under a vacuum. A Chlorex plant of this design, for treating 1000 barrels of oil per day, will require a total ground space not over 50 feet square. From 15,000 to 20,000 gallons of solvent is adequate to place such a plant in operation.

Four Chlorex plants using stills already available in the refinery for recovering the solvent were built at an out-of-pocket cost averaging $41 per barrel of combined charging capacity. A 1000-barrel per day plant using distillation equipment of this type could, therefore, be installed for around $40,000. Five-hundred-barrel-per-day plants built new from the ground up, incorporating continuous vacuum distillation equipment for recovering the solvent, may be installed at a price range from $120 to $180 per barrel charging capacity; while a 1000-barrel-per-day plant can be built for between $80 and $110 per barrel charging capacity. Operating costs in plants with continuous vacuum distillation equipment will run from 0.4 to 0.5 cents per gallon of oil charged, which includes steam, water, electricity, fuel, Chlorex, loss, maintenance, depreciation, and labor.

ACKNOWLEDGMENT

The author wishes to express appreciation to Standard Oil Company (Indiana), especially to F. F. Diwoky, and to the Mid-Continent Petroleum Corporation for the experimental extractions reported herein, and for helpful criticisms and suggestions during the preparation of the manuscript, and to Socony-Vacuum Oil Company, Inc., The Pennzoil Company, Freedom Oil Works Company, and the Bradford Penn Refining Corporation for permitting publication of certain details regarding their Chlorex plant installations.

The Performance and Flexibility of the Duo-Sol Process

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IN the refining of lubricating oil it is shown that conventional methods lack flexibility, and are limited as to quality and yield of product. Some improvement is obtained by counterflow treatment with naphthenic solvents, but this method is limited by characteristics of raw stock in their effect on quality and yield of finished oil. The Duo-Sol process, by counterflow use of propane and naphthenic solvent, introduces a new principle of extraction which permits operation on any lubricating oil stock, regardless of source, to produce oils of highest quality both as to viscosity index and also as regards stability. Stability of Duo-Sol oils is compared, by the Indiana oxidation method and by engine tests, with that of solvent-treated and conventionally refined oils. The article is illustrated by photographs of engine parts after test runs.

This paper was presented at Fifth Mid-Year Meeting, American Petroleum Institute, Tulsa, May 16, 1935.

THE refiner is continually faced by the demand for better products at a lower price. This is a problem that can only be solved profitably by the adoption of refining methods which give a higher yield of the better product or permit operation on cheaper stocks. It is interesting, for this reason, to study the development of refining methods—especially in their relation to quality, yield, and flexibility.

SEPARATION BY DISTILLATION

In the early days of oil refining the chief demand was for burning oils and cylinder stocks, and there was but little demand for gasoline and other fractions. Batch distillation, with little or no fractionation, was suitable for the job of producing these materials—especially since only the highest quality crudes were refined, and since there was little competition for supplying the market. The discovery of lower quality crudes and the growing demand for petroleum products encouraged a competition which resulted in the installation of refineries for operation on the lower grade stocks, and necessitated the use not only of separation by distillation, but of separation by chemical treatment. Demand for new products and greater quantities encouraged the development of more efficient distilling methods, and the continuous shell still battery came into use—and with it came dephlegmators, partial condensers, baffle towers, and other inefficient types of rectifying apparatus. With the adoption of the bubble deck and controlled reflux, the rectifying columns reached a high efficiency. The final development was not made, however, until a new principle was employed. The shell still with its rectifying column was discarded for the tube still and fractionating column—which provided not only rectification, but stripping as well. It was then possible not only to manufacture products of higher quality, but also to increase yield. But, with even the most efficient distilling apparatus, it was found that—except for boiling range—the characteristics of the product and the yield were governed by the nature of the crude from which the product was recovered.

SEPARATION BY SOLVENTS

In the early days of refining burning oils, it became apparent that distillation—which was limited to separation by boiling point—could not be used for removing those impurities which had the same boiling range as the kerosene. It was found that treatment with sulfuric acid improved the burning quality by the removal of aromatics and sulfur compounds, but the treatment resulted in chemical reactions and the formation of a sludge of little value. It was discovered by Edeleanu that liquid sulfur oxide was effective in removing aromatics and sulfur compounds, and could be recovered for re-use. This was a notable advance in the treatment of petroleum fractions, because it employed the principle of selective solubility and avoided chemical reaction which accompanied treatment by sulfuric acid. Thus, a new principle was introduced, which has been a valuable tool to the refiner in the treatment of particular fractions and the production of definite products.

As in the production of gasoline, the automobile created a growing demand for lubricating oils in larger quantity and of higher quality. Following the earlier practices, the attempt was first made to supply this demand, by distillation of high quality crudes, and with such stocks it was possible to make lubricants good enough, for the early needs, by the use of only three separating steps: 1, the separation of the low- from the high-boiling fractions by distillation; 2, the separation of wax by pressing and cold settling; and, 3, the separation of color material by filtration. Again competition and growing demand brought about the manufacture of lubricants from lower quality crudes; and distillation, dewaxing, and filtration were no longer able to supply oils of high enough quality to meet requirements. Acid treatment was resorted to for the removal of the more unstable compounds from both the residual oils and overhead stocks. For a while lubricants produced in this manner found a market, but always at a price lower than that for the oils from the high quality crudes; for, even with the maximum refinement by sul-

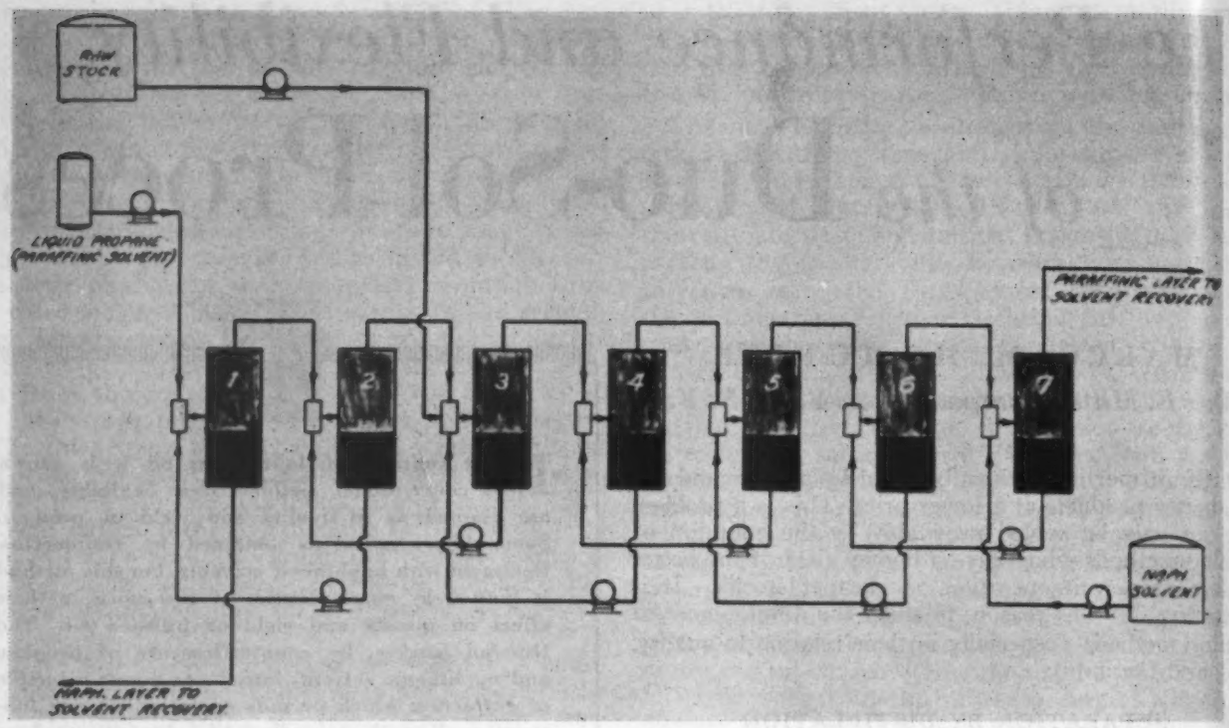

FIGURE 1
Flow Diagram—Duo-Sol Extraction System

furic acid, the quality of the finished oil was limited by the quality of the crude from which it was made. To improve this quality, crudes were segregated, premiums were paid for the better grades—and the poorer stocks, finding no demand for lubricating oil manufacture, were either cracked or their heavy fractions sold as fuel oil.

An attempt was made to improve the quality of lubricants by distillation. It was assumed that, since the residual fraction of lower grade crudes is invariably black and asphaltic, high vacuum distillation would permit the production of lubricants not only of lower asphaltic content, but superior in quality as well. It is safe to say that high vacuum distillation in the production of lubricating oils was responsible for producing oils having a lower carbon residue and requiring less chemical treatment; but it is also safe to say that such oils were less stable, less effective in eliminating wear, and resulted in higher oil consumption. Furthermore, the quality of the overhead lubricant from the lower grade stocks was such that these oils could only find a market at a price below that of the oils from high quality crudes.

The very recent developments in automotive and aviation engines in the way of increased engine speeds, pressures, and temperatures showed that the lubricants from even the highest quality crudes were lacking in stability; and, following the example set by Edeleanu an attempt was made to treat lubricating oil fractions with sulfur dioxide. It was found that this operation was not only difficult because of low solubility and poor settling rates, but that the product was little better than that which was produced by distillation and acid treatment.

Using the same principle of treatment as was introduced by Edeleanu for treating kerosene, numerous solvents were investigated as substitutes for sulfur dioxide. The search for improved solvents resulted in the adoption of phenol, nitrobenzene, furfural, and chlorex for the treatment of lubricating oil fractions. Many others have been proposed; but it is found that no solvent yet discovered used in the manner of Edeleanu can produce from the whole lubricating oil fraction of the crude, and without regard to the quality of the crude, lubricants meeting the highest quality requirements. In fact, most of the solvents proposed are limited to the treatment of particular fractions from crudes of definite characteristics; for example, a solvent which is ineffective in lowering the carbon residue and in the removal of coloring material is limited to the treatment of distillates. The solvent which is ineffective for the removal of sulfur must be used for the treatment of sweet stocks. In similar manner, the use of the solvent is governed by crude characteristics such as naphthenicity, specific gravity, and viscosity. Aside from the limited field for single-solvent extraction, both because of the nature of the stock to be treated and the quality of the product desired, it is found that the counterflow treatment of a stock with a solvent invariably results in the loss of good oil in the extract. This is a fundamental limitation of this type of system, since it is necessary that the extract be removed in equilibrium with the feed. The endeavor today, in single-solvents extraction, as in the time of Edeleanu, is to find a better solvent; whereas the real improvement in the art lies not in a better solvent, but in a new system.

DUO-SOL EXTRACTION—A NEW SOLVENT SYSTEM

Such a system is provided by the Duo-Sol process; and just as modern fractionation—by providing both rectification and stripping to the art of distillation—added improvement in quality, flexibility, and yield, so the Duo-Sol process produces the highest quality product with maximum yield with unlimited flexibility as to the selection of stocks to be treated. The basic principle of the Duo-Sol process is that propane as a paraffinic solvent may be used in conjunction with a

naphthenic solvent to accomplish three purposes—the first being by simultaneous use, to increase the selectivity of the separation; the second, to provide a stripping section so that fractionation by solvents may have the elements required for maximum quality and yield, viz., rectification and stripping; and the third, to make the extraction system independent of the characteristics of the charging stock whether because of naphthenicity, specific gravity, viscosity, boiling range, or nature of impurity.

Five years ago this new principle of extraction was an idea. For three years practical methods of employing the principle were studied in the laboratory (see Figure 1). Two years ago a pilot plant (Figure 2) was built for continuous operation, and for the first time untreated stocks were continuously extracted by the simultaneous counterflow of propane with a naphthenic solvent. Last year three plants were put into operation, having a daily output of Duo-Sol-treated oil of over 6000 barrels a day, and construction was started on two

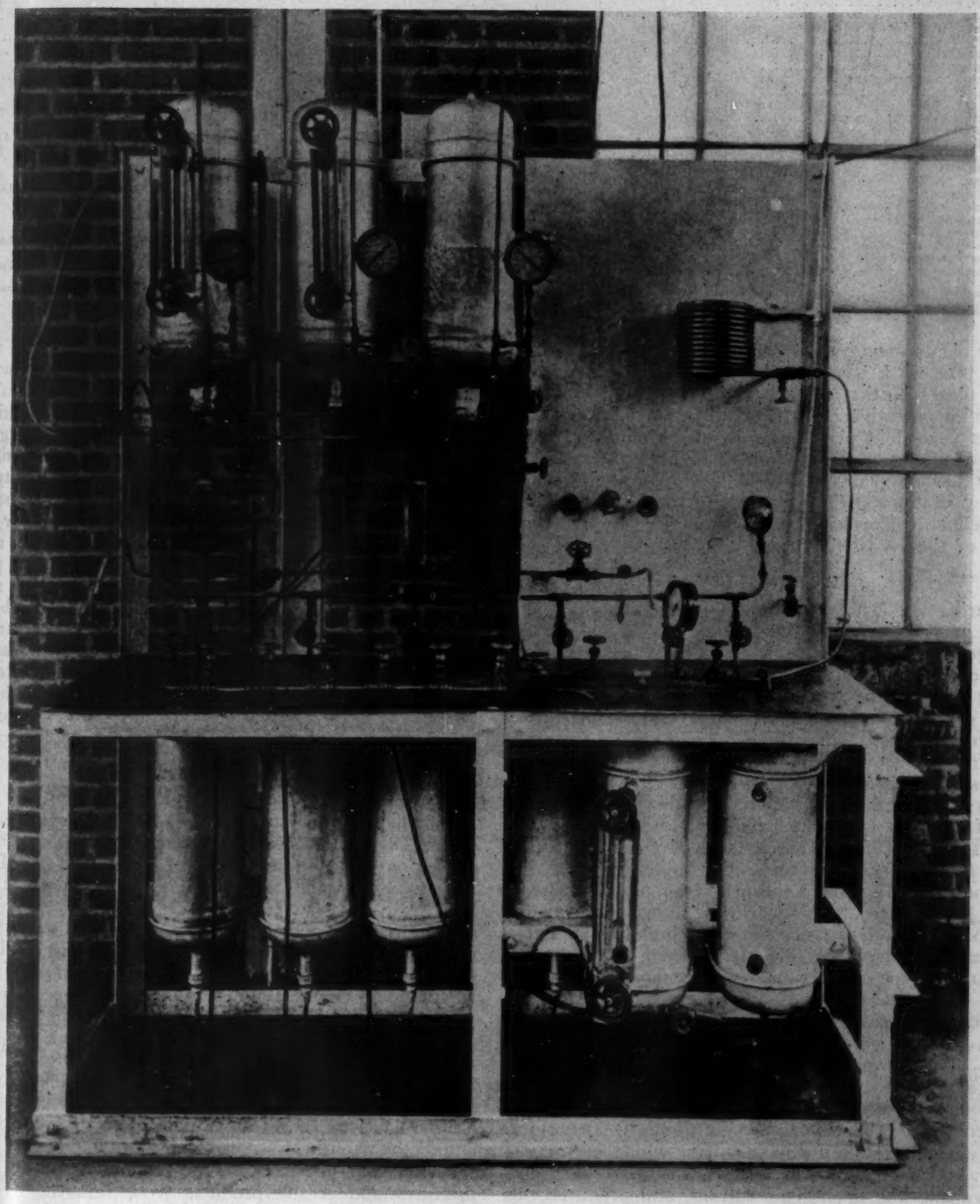

FIGURE 2
Laboratory Extractors

TABLE 1

OIL SPECIFICATIONS	Pennsylvania Cylinder Stock	Pennsylvania Long Residuum	Ranger-Burbank Residuum	Deep-Sand Reagan Residuum	Iraq Residuum	Coastal Neutral	San Joaquin Distillate	Panhandle Overhead (Dewaxed)	Mid-Continent Steam-refined Stock	Kansas Long Residuum	Hendricks Residuum	Mid-Continent Neutral
Charging Stock:												
Gravity, ° API	25.6	28.6	23.5	22.4	14.8	18.8	16.3	22.9	21.1	18.6	16.8	25.4
Specific gravity	0.9007	0.8838	0.9129	0.9194	0.9674	0.9415	0.9574	0.9165	0.9273	0.9427	0.9541	0.9018
Viscosity at 210° F., sec.	165	70	84	205	194	51	96	95	197	154	147	48
Flash point, ° F.	560	435	450	555	420	350	465	520	530	485	455	430
Fire point, ° F.	625	465	500	625	470	385	525	585	600	570	500	485
Viscosity-gravity constant	0.8135	0.8080	0.8480	0.8350	0.8990	0.8945	0.8970	0.8445	0.8465	0.8700	0.8860	0.8520
Solvent Rates:												
Selecto, percent	400	400	300	325	300	125	800	225	125	400	275	300
Propane, percent	200	300	350	250	400	250	300	200	400	300	250	150
Paraffinic Oil Before Dewaxing:												
Gravity, ° API	28.6	30.9	29.9	28.1	29.1	.....	30.8	.....	25.2	29.5	27.6	.....
Specific gravity	0.8838	0.8713	0.8767	0.8866	0.8811	.....	0.8718	.....	0.9030	0.8789	0.8894	.....
Viscosity at 210° F., sec.	122	61.5	61	121.5	53	.....	53.6	.....	123	66.5	67	.....
Viscosity-gravity constant	0.7960	0.7950	0.8030	0.8000	0.8130	.....	0.7990	.....	0.8210	0.8035	0.8170	.....
Color, NPA	70-30-7½	7½	5½	8	3½	3	1¾	4¾	7½	8+	4½	3¼
Yield of paraffinic oil before dewaxing with relation to charge, percent	88.1	92	78.4	76.9	55	91.3	25.4	79.5	85.8	59.5	49.3	78.3
Naphthenic Fraction:												
Specific gravity	1.026	1.027	1.045	1.029	1.073	1.060	0.9865	1.037	1.075	1.037	1.017	1.015
Yield of tar with relation to charge, percent	11.9	8	21.6	23.1	45	8.7	74.6	20.5	14.2	40.5	50.7	21.7
Dewaxed Oil:												
Gravity, ° API	27.8	30.0	29.0	27.3	27.6	20.6	30.7	28.3	24.5	29.1	27.5	31.1
Specific gravity	0.8883	0.8762	0.8816	0.8911	0.8894	0.9303	0.8724	0.8855	0.9071	0.8811	0.8899	0.8702
Viscosity at 100° F., sec.	1,625	451	509	1,930	324	316	341	667	2,700	515	580	178
Viscosity at 210° F., sec.	126.5	63.5	65	133.2	54.2	47.5	54.5	72.5	138.5	66	67	97*
Pour point, ° F.	0	5	20	10	5	—5	10	10	10	5	0	5
Viscosity-gravity constant	0.8010	0.8010	0.8100	0.8044	0.8220	0.8830	0.8003	0.8085	0.8250	0.8060	0.8170	0.8150
Viscosity index	106	108	100	99.5	100	15	95	97	78.5	103	94	100
Carbon residue, percent	0.68	0.38	0.23	0.446	0.17	Trace	0.02	0.20	1.0	0.20	0.15	Trace

* At 130° F. NOTE.—Color indicated is that produced by Duo-Sol processing without color treatment.

other plants—one in this country and one in England. This year work has started on three additional European plants, so that at present there are eight Duo-Sol plants in operation or in course of construction. The stocks treated in plants now in operation range from light distillates to residual oils of high viscosity, and in every case the quality and yield have duplicated the pilot plant operation. It is safe, then, to consider pilot plant as well as commercial runs in studying the performance of the Duo-Sol process.

FLEXIBILITY

During the last two years the pilot plant has been kept in practically continuous operation, and in the course of that time some 75 stocks have been run. An idea of the flexibility of the process, as to the kind of stock that can be treated, is indicated by these runs. The stocks include distillates and residual oils. Oils varying in flash point from 375 °F. to 600 °F.—ranging from light overheads to a vacuum still tar having a viscosity of 1375 at 210 °F.; from a 29 API distillate to tars heavier than the naphthenic solvent; from highly paraffinic oils to stocks having viscosity-gravity constants above 0.95, and stocks derived from crudes not only from every important section of this country, but extending to oils from Venezuela, Iraq, and Germany—have been treated. This work has shown that, regardless of the source of crude—whether high in wax, naphthenes, asphaltenes or sulfur compounds—and regardless of the type of fraction—whether distillate or residuum—the Duo-Sol treated oils have unusual stability, a low carbon residue—and even from such high sulfur stocks as Iraq, a sulfur content too small to be measured. The color improvement is so great that the treated oil may be brought economically to color by clay treatment without the use of acid. Wide latitude is permitted in the control of the viscosity index of the treated stock. For example, a California distillate which had a viscosity index of —50 was treated with different ratios of propane and naphthenic solvent, and produced oils ranging in viscosity index from 40 to 100. Further examples of stocks handled, together with yield and quality of finished oils, are given in Table 1.

The ability of the Duo-Sol process to handle any lubricating oil fraction from any crude for the removal of unstable sludge forming material, for the removal of naphthenic acids, sulfur compounds, and those fractions which are of low viscosity index, without loss of good oil, is of major importance. Such flexibility permits a wide choice as to crude supply and great flexibility as to the quality of the oil produced. From the same stock oils of high, intermediate, or low viscosity index, or oils meeting special requirements as to stability, carbon residue, sulfur, and naphthenic acid content, may be produced. The same plant without change in solvents may be used for increasing the viscosity index and stability of a distillate, for decreasing the viscosity and carbon residue of a residual oil, and at the same time increasing its stability, viscosity index, and improving its color. This reduction in viscosity of residual oils, through the removal of extremely viscous tars and resins, is becoming of greater importance as the demand for lubricants of lower viscosity increases.

PRINCIPLE OF DUO-SOL PROCESS

In order to understand the reason for the flexibility of the Duo-Sol process, it is necessary to consider the extraction principle involved (see Figure 3). The Duo-Sol process provides an extraction system in which two liquid solvents are employed, each having a limited miscibility in the other, and one a selective solvent action for the more paraffinic crude fractions, and the other a selective solvent action for the non-paraffinic fractions. A counterflow is established between the two solvents, and to them the raw stock is fed at an intermediate point. At the feed point the stock is selectively dissolved by the solvents, and equilibrium established between the paraffinic and naphthenic layers. Equilibrium at the feed results in an enrichment of the paraffinic layer by oil more paraffinic than the feed, and of the naphthenic layer by oil more naphthenic than the feed; but in each case the material dissolved is a mixture—and if the products were removed at this point, the naphthenic layer would contain good paraffinic oil with resultant loss in yield, and the paraffinic layer would contain naphthenic material with resultant

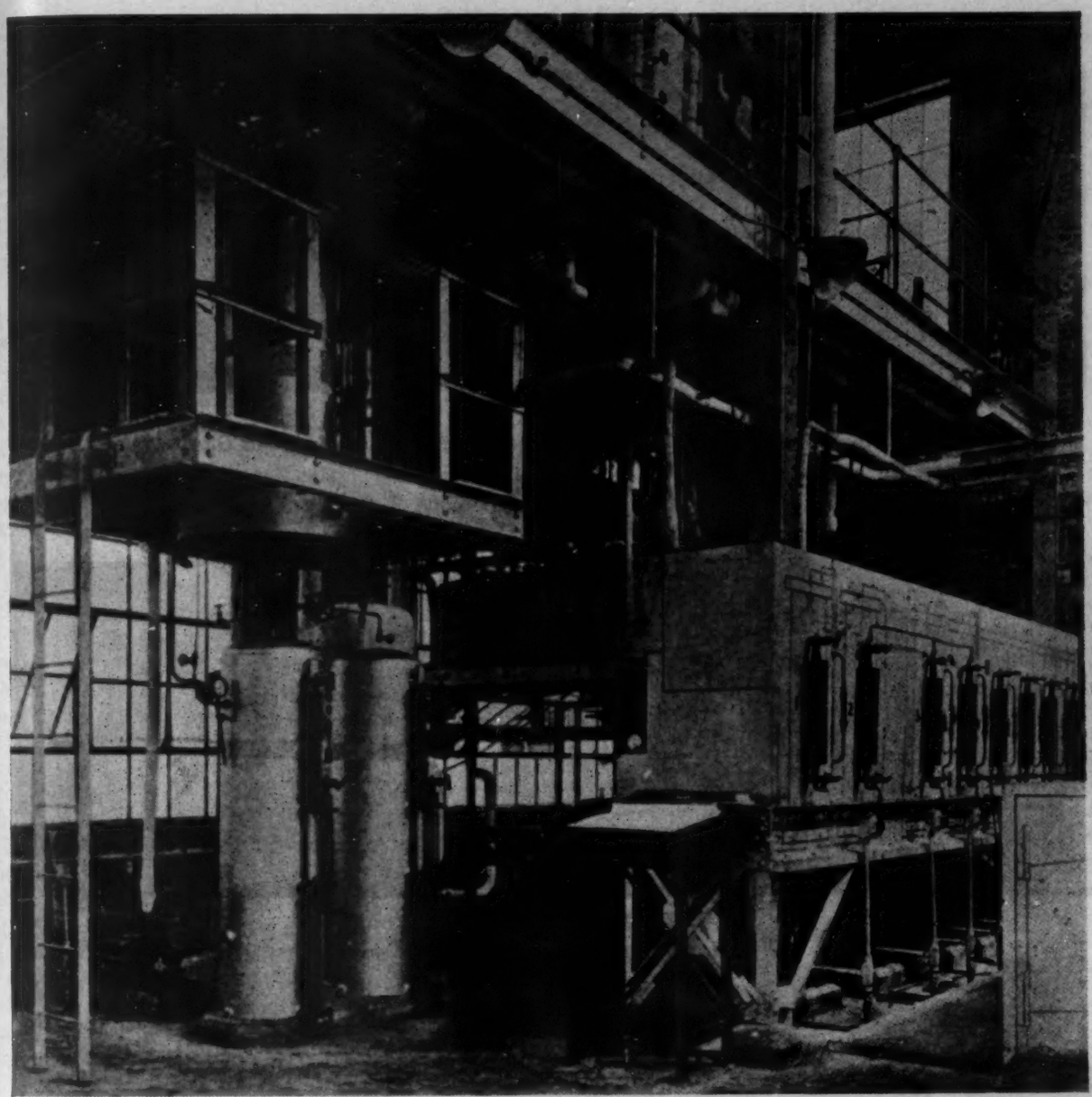

FIGURE 3
Duo-Sol Pilot Plant

loss in quality. To recover the paraffinic oil contained in the naphthenic layer, equilibrium is established in two successive stages between the outgoing naphthenic layer and the incoming propane. To remove naphthenic material contained in the paraffinic layer, four successive stages of equilibrium are established with the incoming naphthenic solvent. Counting the feed stage, there are seven stages of contact and equilibrium —of which four are effective in rectifying the paraffinic layer, and two effective in stripping the naphthenic layer. It may be seen that the Duo-Sol process employs a naphthenic solvent and a paraffinic solvent, and provides an extraction system consisting of a feed section, a rectifying section, and a stripping section. The rectifying section makes possible the production of oil of high quality, and the stripping section prevents loss of good oil.

This was the Duo-Sol idea of five years ago, and it has resulted in providing to plant operation a flexibility as to stocks handled and quality of oils produced that was non-existent before that time.

CHOICE OF NAPHTHENIC SOLVENT

In the selection of a naphthenic solvent to be used in conjunction with propane in the Duo-Sol process, it is necessary to consider a number of factors.

The solvent should have a limited miscibility with propane in the presence of oil. It should not only have a high solubility for non-paraffinic compounds, but also some solubility for paraffinic material. The critical-solution temperature should be in the range of 120 °F. to 160 °F., so as to permit operation at normal temperatures and pressures. Its selectivity for naphthenic oil should be increased by the presence of propane. It must be stable not only during extraction, but also during recovery and storage. Its final boiling point should not exceed 425 °F. It should have a high specific gravity, so as to promote rapid separation be-

FIGURE 4
Valve Chamber of Mack Bus Engine After 200 Hours Using SAE-60 Pennsylvania Oil—Process "A"

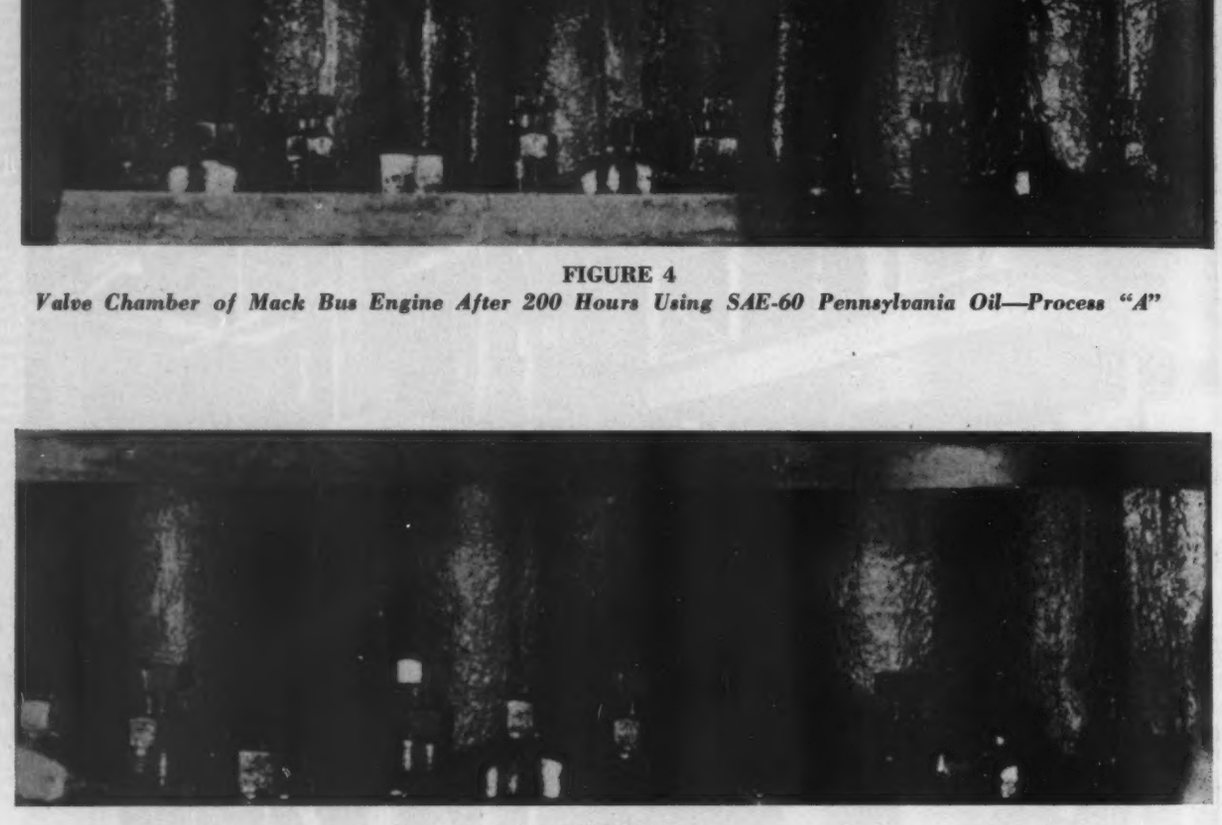

FIGURE 5
Valve Chamber of Mack Bus Engine After 200 Hours Using SAE-60 Duo Sol Oil

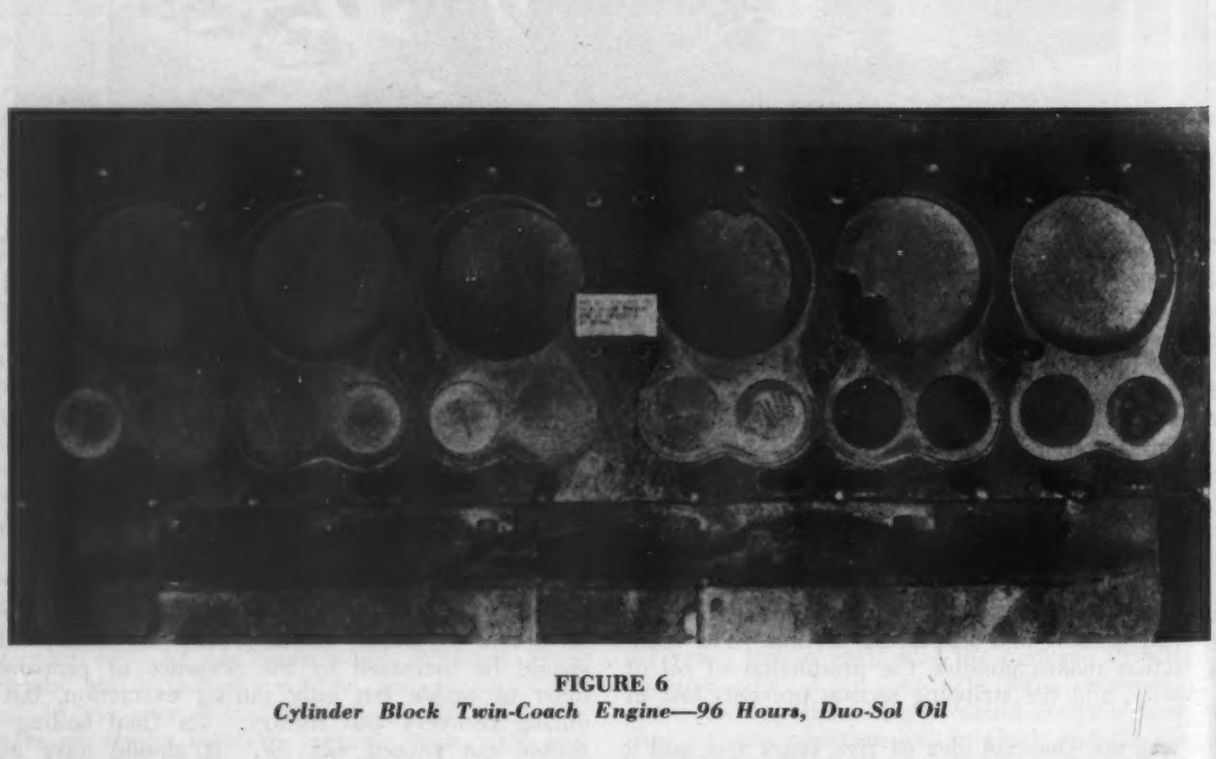

FIGURE 6
Cylinder Block Twin-Coach Engine—96 Hours, Duo-Sol Oil

TABLE 2
Oxidation of SAE-40 Oils

CRUDE SOURCE	PROCESS	BEFORE OXIDATION			AFTER OXIDATION 100 HOURS AT 350° F.		
		Viscosity Index	Viscosity at 210° F. (Seconds)	Carbon Residue (Percent)	Viscosity at 210° F. (Seconds)	Carbon Residue (Percent)	Sludge (Milligrams)
Mid-Continent residuum	Duo-Sol	100	76	0.33	85	1.12	None
Mid-Continent overhead	Single Solvent	87.5	73	0.20	84.5	1.45	68
Pennsylvania	Conventional	100	75	0.60	119	3.36	43
Pennsylvania	"A"	105.7	72.5	0.23	85	1.05	19
Coastal	Conventional	0	62	0.09	104	2.54	100*

*100 mg. after 41 hours.

tween the layers. It should have a low melting point, so as to avoid crystallization during extraction or storage. It should be reasonable in price, and available in large quantity.

A thorough investigation of organic solvents indicates that cresylic acid most nearly meets the above requirements, and this material is the chief constituent of the naphthenic solvent called "Selecto" used in the Duo-Sol process.

As a single solvent, it has found little use because of its low critical-solution temperatures with mixed-base stocks, and because of its relatively high solubility for not only all of the non-paraffinic components, but the paraffinic as well. With highly naphthenic stocks, and with those of high specific gravity or high viscosity, separation is so poor as to make its use impractical, if not impossible. But with all its shortcomings as a single solvent, it has a very valuable characteristic when used in counter-current with propane—and that is its ability to take all of the non-paraffinic material into solution. Such paraffinic material as also goes into solution is of minor importance, since this is recovered by propane in the stripping section.

It is also found that the simultaneous use of propane and cresylic acid improves the selectivity of extraction; for example, a dewaxed Oklahoma City residuum when batch-treated with 300 percent Selecto produces a paraffinic layer of 68.65 percent, which is made up of 59.63 percent paraffinic oil and 9.02 percent naphthenic oil. When the same oil is treated with 300 percent Selecto and 300 percent propane, a paraffinic layer is produced amounting to 77.77 percent, which contains 65.29 percent paraffinic oil and 12.48 percent naphthenic oil. If the ratio of paraffinic oil in the paraffinic layer to paraffinic oil in the naphthenic layer is determined just as the $\frac{Y}{X}$ ratio is determined in separation by distillation, it is found that the $\frac{Y}{X}$ for the treatment with 300 percent Selecto is 2.48, while the $\frac{Y}{X}$ for the treatment with 300 percent Selecto and 300 percent propane is 3.49. Furthermore, it is shown that the yield by the Duo-Sol process is 70.60 percent, while by the single-solvent method it is 59.63 percent. Aside from the difference in yields, there is a decided difference in the quality of the two oils; as it is found that for oils of the same viscosity index the Duo-Sol-treated oil has a better color, a lower carbon residue, and a greater resistance to oxidation than the oil treated by the single solvent alone.

RESISTANCE TO OXIDATION

As an indication of the stability of the Duo-Sol-treated oils, a comparison has been made between SAE-40 Duo-Sol oils and other commercial lubricants of the same grade before and after an Indiana oxidation test, run in each case for a period of 100 hours. These tests, Table 2, show clearly that the Duo-Sol process produces oils which are not only high in viscosity index, but are extremely stable to oxidation as well. Furthermore, it shows that the carbon residue of the unoxidized oil is no indication of the carbon residue after oxidation. For example, the single-solvent-treated Mid-Continent overhead with an initial carbon residue of 0.20 had a carbon residue after 100 hours of 1.45; while the Duo-Sol oil with a higher initial carbon residue had, after 100 hours, a carbon residue of 1.12. Furthermore, the Pennsylvania oil with an initial carbon residue of 0.60 had 3.36 after 100 hours. It should also be noted that the increase in viscosity and the amount of sludge precipitated indicate a greater stability for Duo-Sol oils than for any of the other oils.

PERFORMANCE TESTS

While laboratory examination of the finished oils is of interest, the final measure of the quality of lubricating oil is by actual use. The tendency of an oil to form and deposit sludge or carbon in an engine and the rate of oil consumption can only be determined by actual engine tests. Numerous engine tests have been made in which Duo-Sol oils have been compared with the highest quality oils obtainable, and in every case it is shown that sludge and carbon formation and oil consumption are reduced. There have also been less wear and less sticking of rings and fouling of valves.

Figure 4 shows the valve chamber of a Mack bus engine after a run of 200 hours using an SAE-60 Pennsylvania oil refined by special process "A." Figure 5 shows the same engine at the end of a similar run using Duo-Sol-treated SAE-60 oil. By actual measurement, there was five times as much sludge deposited in the valve chambers by the special Pennsylvania oil than there was by the Duo-Sol-treated oil.

Figure 6 shows the cylinder block of a twin-coach bus engine after a 96-hour run using Duo-Sol-treated oil, and Figure 7 shows a piston from the engine at the end of the same run. The remarkable cleanliness of the engine is apparent.

In order to provide more extreme conditions, the single-cylinder engine illustrated in Figure 8 was developed. In this engine the cylinder jacket is maintained at a temperature of 350 °F., using glycol in place of

FIGURE 7—*Piston of Twin-Coach Engine—96 Hours, Duo-Sol Oil.*

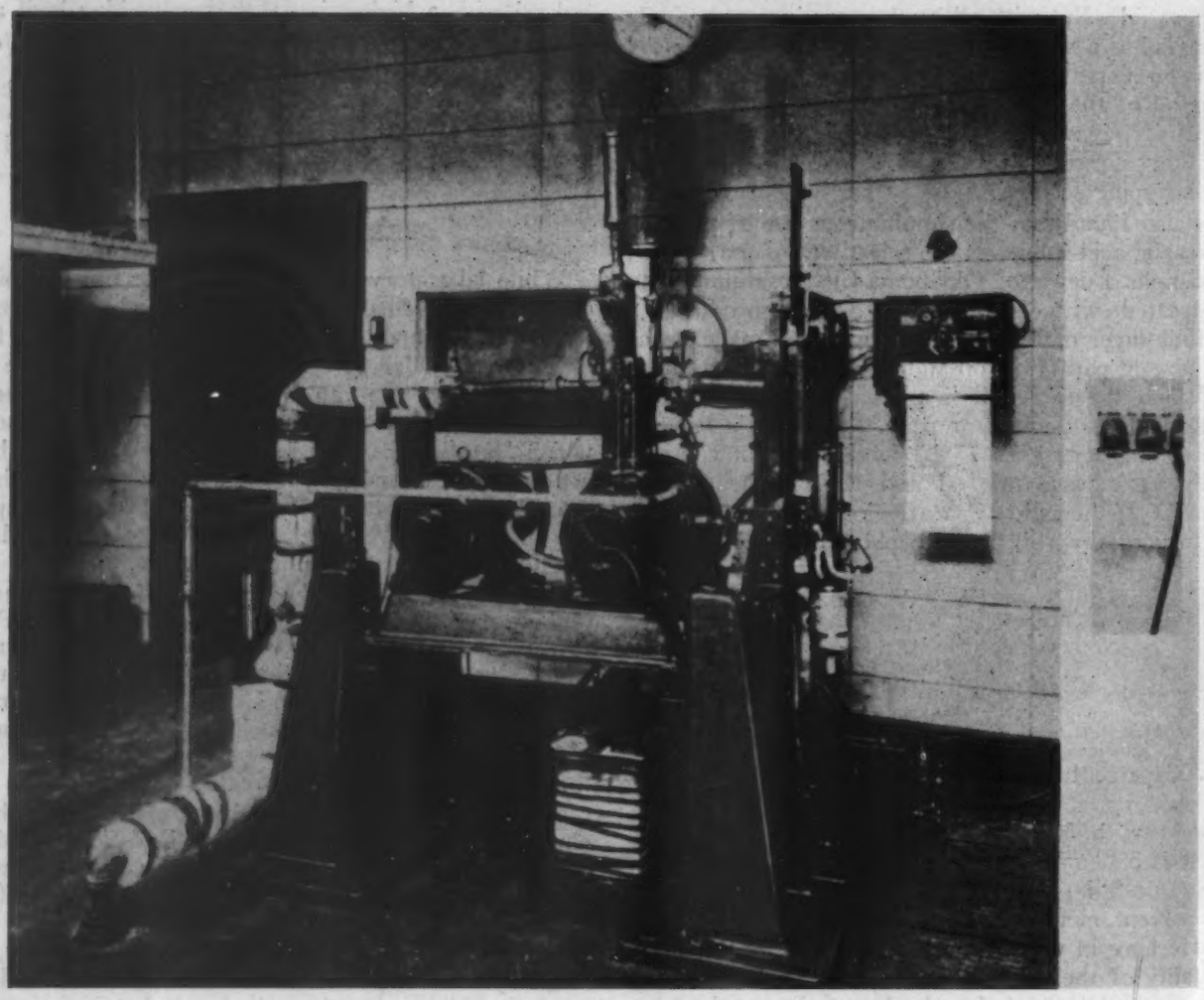

FIGURE 8—*Single-Cylinder Test Engine—Glycol-cooled.*

FIGURE 9
Test-Engine Piston—Pennsylvania Oil, Process "A"—100 Hours

FIGURE 10
Test-Engine—Synthetic Oil, 73 Hours

FIGURE 11
Test-Engine—Compounded Oil, 100 Hours

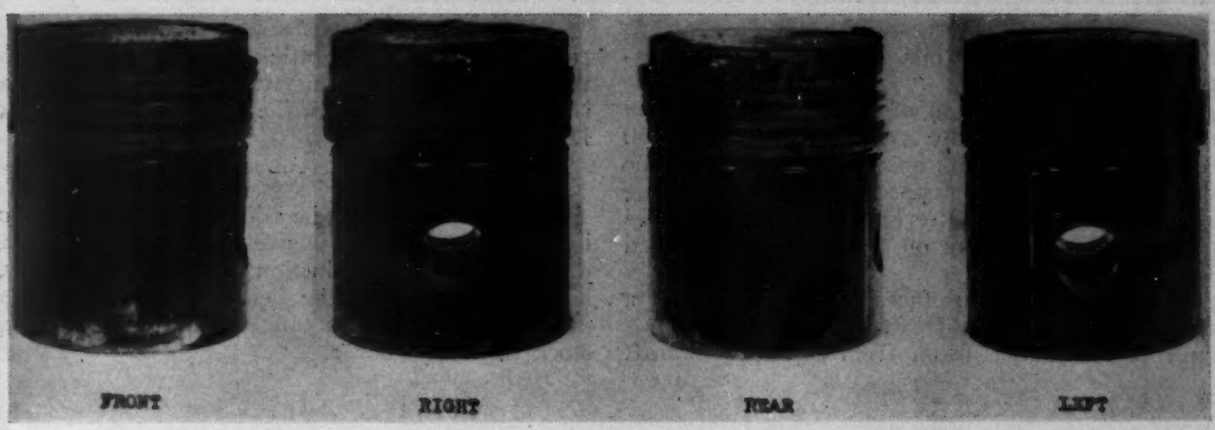

FIGURE 12
Test-Engine—Duo-Sol Oil, 100 Hours

FIGURE 13
From Jacobs Aircraft Engine—Pennsylvania Aviation Oil, Full Throttle, 50 Hours

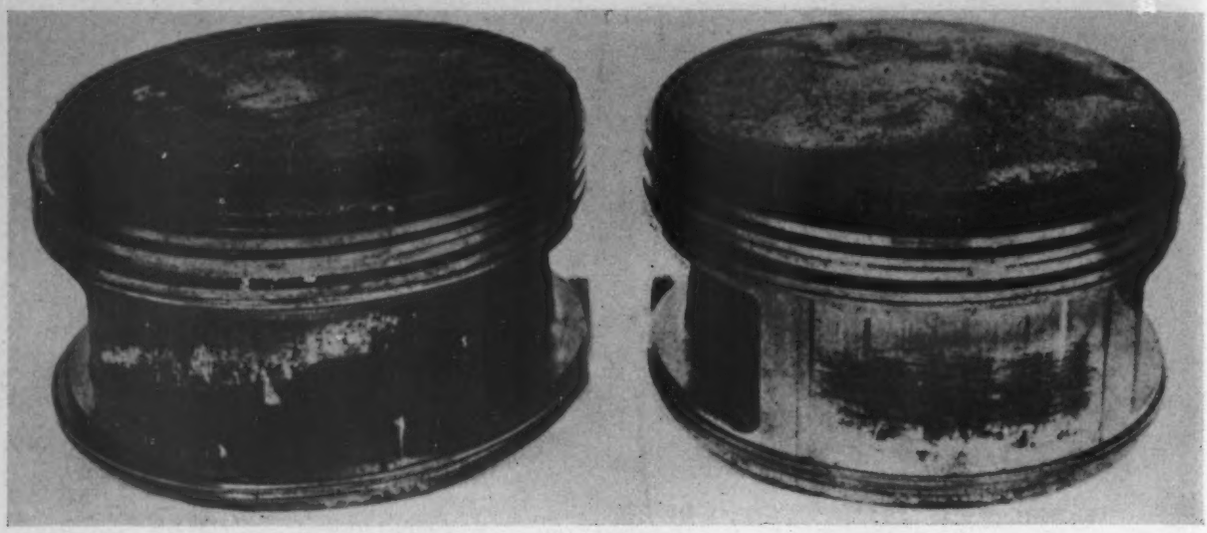

FIGURE 14
From Jacobs Aircraft Engine—Duo-Sol Oil, Full Throttle, 50 Hours

water for cooling. Various oils were used in camparative tests with Duo-Sol oil.

Figure 9 shows the piston after a 100-hour run on Pennsylvania oil refined by process "A." Figure 10 shows the piston after a run on a commercial synthetic oil, which run had to be stopped at 73 hours because of scoring of the piston and cylinder. Figure 11 shows the piston after 100 hours on a special compounded aviation oil.

Figure 12 shows the four faces of the piston after a 100-hour run with Duo-Sol-treated oil.

Figure 13 shows the piston from a Jacobs aircraft engine run at full throttle for 50 hours with a conventionally-refined Pennsylvania aviation oil. Figure 14 shows the same piston at the end of a similar run using Duo-Sol oil.

CONCLUSION

In conclusion, it may be said that the Duo-Sol process, by providing a new principle of solvent extraction, has made possible the production of higher quality oils, and has greatly extended the field of solvent extraction by making possible the treatment of any lubricating oil stock from any source.

The Refining of Lubricating Oils With Furfural

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The Texas Company

THIS paper describes the operation and development of the furfural refining process as applied commercially to the manufacture of high quality lubricants from distillate stocks derived from Mid-Continent pipe line crude and ranging in viscosity between 40 sec. and 180 sec., Saybolt Universal, at 210°F.

The most recent design of a furfural refining unit is described, and a flow diagram presented. Operations are considered from the standpoint of solvent losses, investment in equipment, operating costs, and product quality.

Solvent losses have been 0.038 percent of the total solvent distilled in the commercial unit.

Direct operating costs have been approximately $0.1739 per barrel of charge to the furfural refining unit.

Investment costs vary between $70 per barrel of daily capacity for the 5000-barrel units to about $300 per barrel for a 500-barrel plant.

Lubricants manufactured by furfural refining have given excellent service performance, and have shown unusually high resistance to oxidation and sludging.

Pilot-unit tests are shown illustrating the application of furfural refining to a variety of lubricating stocks.

This paper was presented at Fifth Mid-Year Meeting, American Petroleum Institute, Tulsa, May 16, 1935.

THE development of the process employing furfural as a selective refining solvent in the manufacture of lubricating oils of improved service characteristics was discussed in a paper presented at the Fourteenth Annual Meeting of the American Petroleum Institute in October, 1933.[1a] In this paper it was pointed out that the ideal refining solvent should effect separation of extract without loss of raffinate constituents, should be stable at the maximum distillation temperatures employed in stripping, and should be applicable to even the highest viscosity oils at temperatures high enough to obtain intimate contact and rapid separation of extract and raffinate solutions in a continuous counter-current application. It was pointed out that the solvent should be available in large quantities at a low cost, and should be relatively non-toxic.

Immediately after the laboratory development had been reported, a commercial plant was completed, and has been in successful commercial operation since December, 1933. This article deals specifically with the commercial application of furfural in the refining of distillate-lubricating stocks derived from Mid-Continent crude.

The original work on furfural refining was covered in U. S. Patent No. 1,550,523, issued to Eichwald.[2] This patent discloses broadly the use of furfural for the purification of hydrocarbon oils. During the year 1931 laboratory work was started to establish the commercial possibility of furfural as a selective refining solvent. This work was continued through 1932 and 1933, and a plant was designed and installed in the refinery of Indian Refining Company at Lawrenceville, Illinois, being completed on November 8, 1933. The plant has been in practically continuous operation at full capacity since that date. It has handled exclusively distillate oils derived from pipe line Mid-Continent crude by vacuum distillation. The oils have ranged in viscosity from 40 sec. Saybolt at 210°F. up to 180 sec. Saybolt at 210°F. These oils have been solvent-dewaxed with acetone-benzol after furfural refining, and subjected to finishing operations for the production of a suitable color and cast.

DESCRIPTION OF PLANT AND OPERATION

Figure 1 is a flow diagram representing the most up-to-date design of a furfural refining unit.

The flow illustrated in Figure 1 has embodied certain features not included in the Lawrenceville plant. The changes to be made in the newer installations have resulted from a more complete study of solvent recovery and stripping operations, and these changes have not affected the basic principles in any way.

The plant consists of the following main operating units, as shown in the flow sheet:

1. A vertical counter-flow extraction tower with pre-heaters and exchangers for furfural and charge oil.
2. Extract-stripping unit for two-stage dry distillation of furfural from extract solution followed by steam stripping under vacuum for removal of final traces of solvent.
3. Refined-oil stripping unit for vacuum distillation of furfural from the refined-oil solution followed by steam stripping under vacuum for removal of final traces of solvent.
4. A solvent-recovery system for recovery of furfural from water.

The unique feature of this plant is the installation and successful operation of a packed counter-flow extraction tower. The use of a counter-flow extraction tower instead of a large number of stages in step counter-flow has been proved to be advantageous from the standpoint of plant investment in equipment, simplified operation, reduced operating and repair costs.

The high temperatures of application of furfural

[a] Figures refer to bibliography on p. 11.

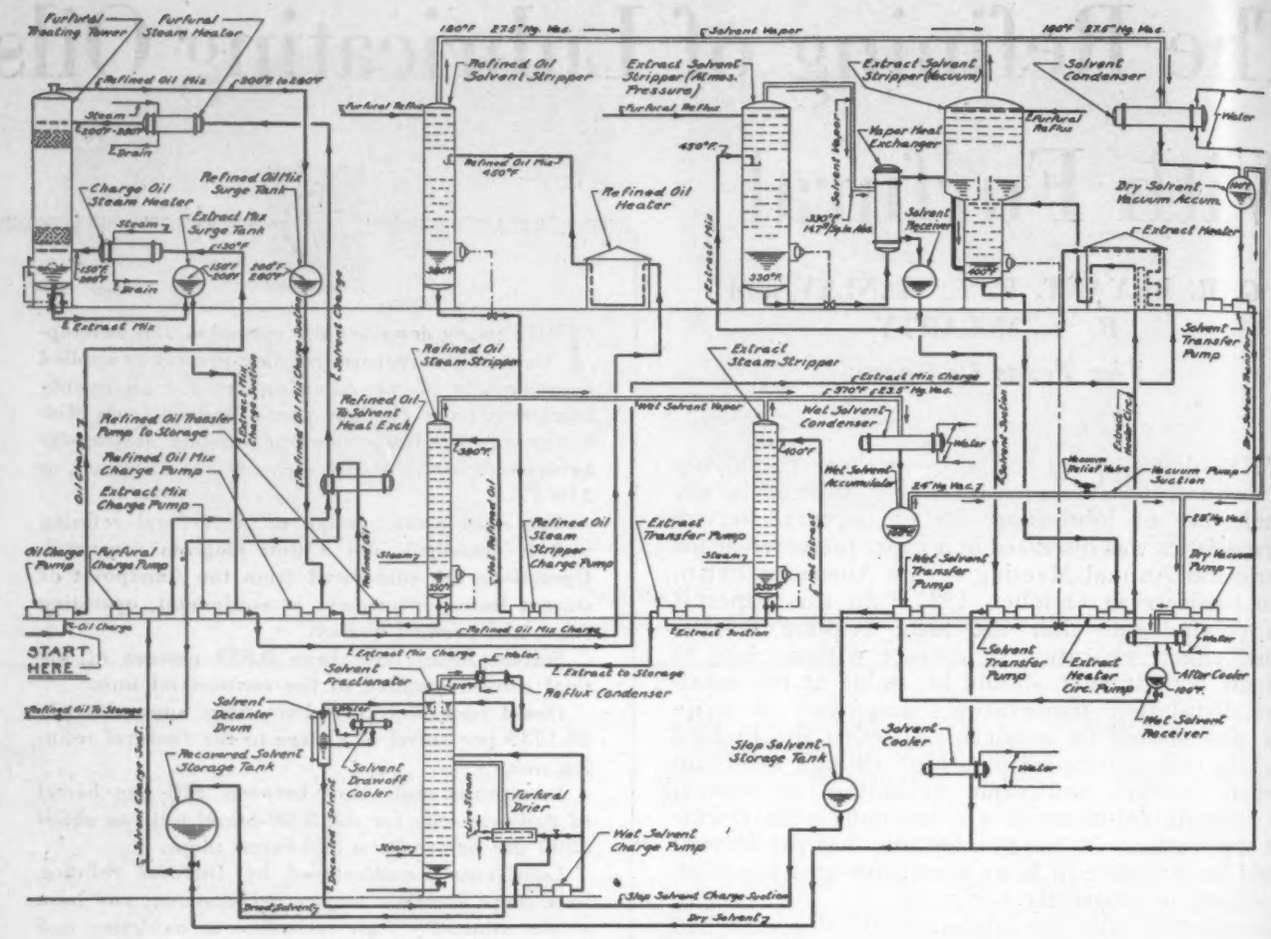


FIGURE 1
Flow Diagram—Furfural Refining Plant.

and the difference in specific gravity between extract and raffinate solutions permit counter-flow operation in a packed tower as well as counter-flow application in multi-stage. Not only are settling rates of furfural in oil very high, but furfural selectively wets stoneware packing, spreading over the surface of the packing in a thin film, and offering a large surface of contact at the interface between the two liquid phases—thus permitting the two phases to approach equilibrium quickly. The high operating temperatures insure a low viscosity in the oil phase and a low resistance to the attainment of equilibrium.

It should be emphasized that furfural is equally adaptable to both counter-flow-tower and step-counter-flow operation. Either system may be used—the choice depending upon the economics involved, the flexibility desired, and the likes and dislikes of the individual refiner.

Referring to Figure 1, raw lubricating stock is charged at a constant flow rate to the bottom of the furfural treating tower through a heater in which temperature is regulated to the desired point. Temperatures range from about 130°F. minimum for low viscosity or naphthenic oils to 220°F. for the high viscosity paraffinic oils.

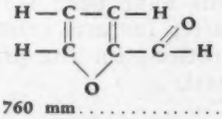
Furfural is charged through a heat exchanger, where heat is recovered from the hot solvent-free refined oil; thence through a live steam heater, where temperature is regulated to the desired point —for low viscosity or naphthenic oils about 160°F. minimum, and about 270-280°F. maximum for high viscosity paraffinic oils.

Temperature gradient has been found to be decidedly advantageous in effecting the desired fractional separation of extract and refined oil; and, in general, it has been found that top tower temperatures determine quality of refined oil, while bottom tower temperatures establish yields.

The extraction tower is packed with about 20 feet of raschig rings, with re-distribution means at about each four feet of packed tower space. Charge rates should average about 35 gallons of charge oil per hour per square foot of over-all tower cross-sectional

PROPERTIES OF FURFURAL

Structural formula:



Boiling point, °F. at 760 mm	323
Freezing point, °F.	—34
Specific gravity at 60°F.	1.164
Kinematic viscosity at 100°F. (centistokes)	0.907
Specific heat (68°F. to 212°F.)	0.416
Heat of vaporization (29.9 in. mercury) B.t.u. per lb.	193.5
Vapor pressure at 100°F., mm	7
Tagliabue closed-cup flash, °F.	138
Solubility of furfural in water at 100°F., percent by weight	8.96
Critical temperature, °F.	746
Critical pressure, lb. per sq. in., absolute	798

area, although rates as high as 70 gallons per square foot per hour have been used without excessive mechanical entrainment of solvent with refined oil.

Provision may be made for external cooling of extract mixture more completely to fractionate refined oil from extract. This may be accomplished by withdrawal of extract mixture through a cooler and re-introduction of the cooled mixture into the lower section of the extraction tower. The use of an external cooler is particularly desirable where high ratios of solvent to charge oil are employed, in order to keep yields of refined oil at a maximum.

Extract mixture and refined oil mixture are withdrawn from the bottom and top of the extractor, respectively. Levels are controlled by a duo-gravity float in the bottom, the continuous phase in the extractor being the oil phase. The separate layers are received in separate surge vessels upon which the extract mixture charge pump and refined-oil mixture charge pump take suction. The mixtures are stripped in the respective solvent recovery systems.

The refined oil mixture is stripped by flashing the solvent from the heated mixture into a vacuum. The amount of solvent passing through this part of the equipment averages about eight percent of the total solvent used. The amount of solvent remaining in the oil after flashing averages about 0.4 percent by weight, and this amount is removed by steaming under a vacuum of about 24 inches of mercury in a steam stripping column. The furfural and water vapors are condensed and pumped to slop solvent, while the dry solvent from the dry vacuum system is pumped directly to recovered solvent for re-use in the furfural treating tower.

The extract mixture is stripped in three stages in order to effect a fuel economy. The first step consists

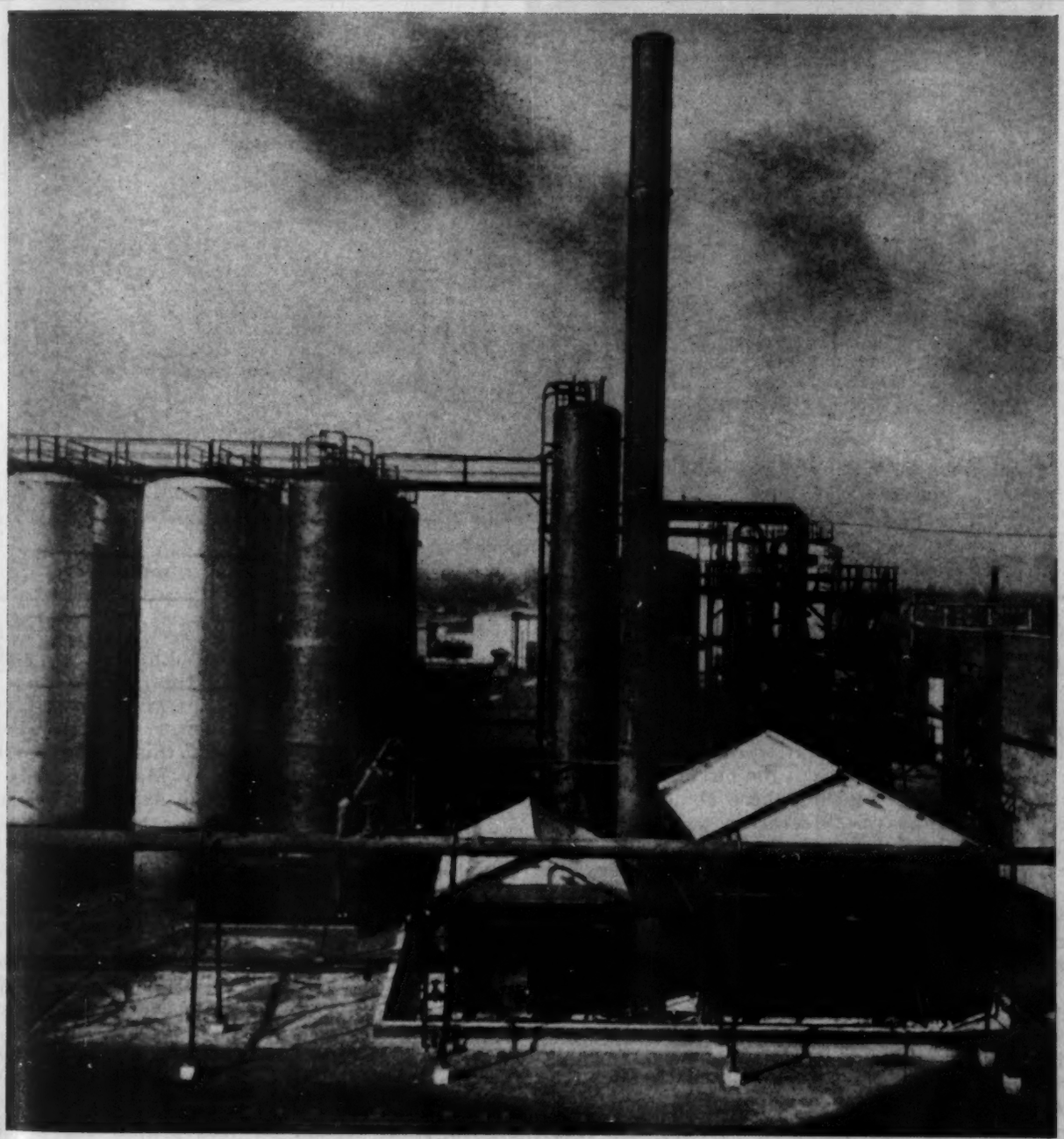


FIGURE 2
Furfural Refining Unit, Indian Refining Company, Lawrenceville, Ill. (Looking North).

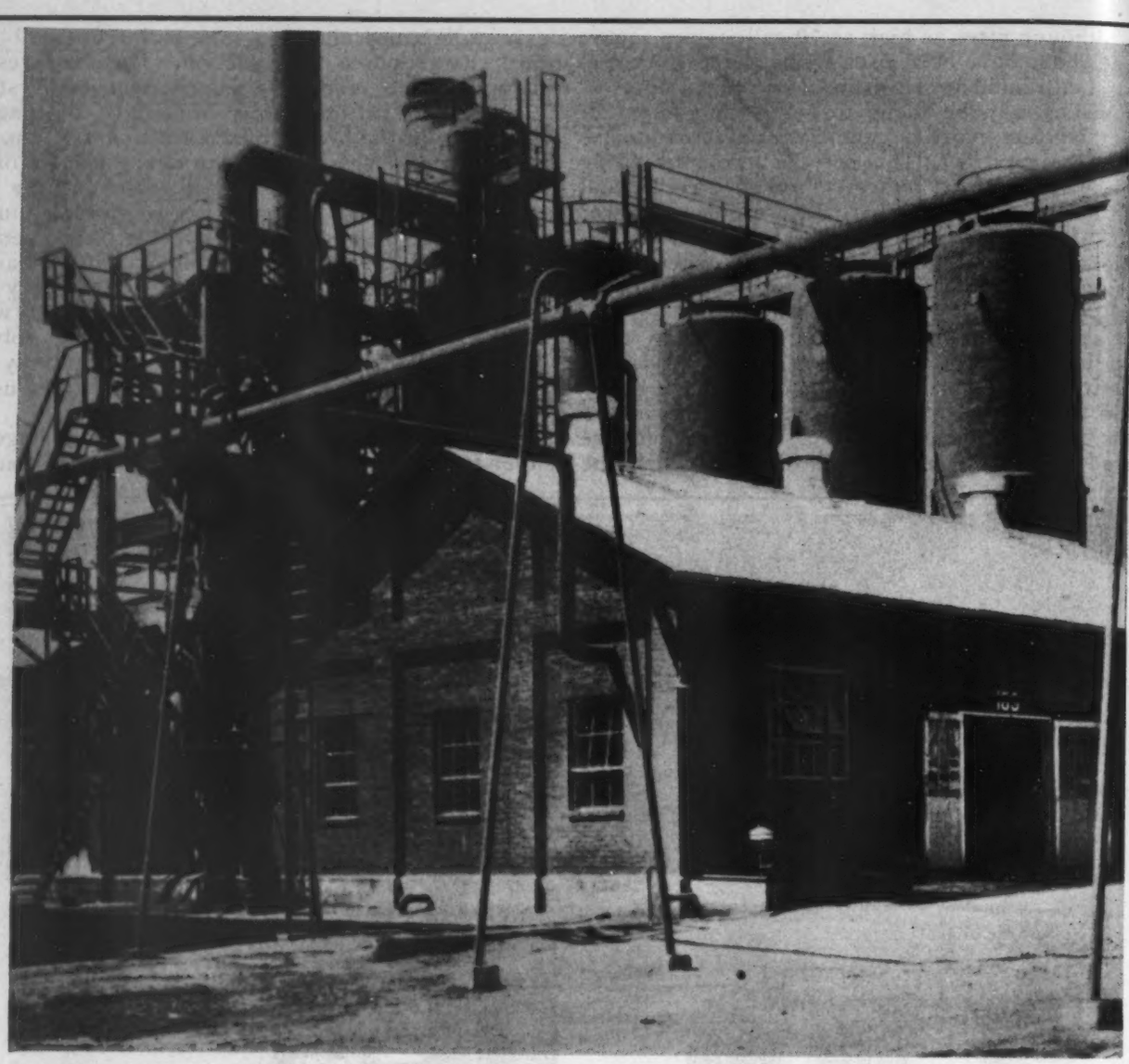


FIGURE 3
Furfural Refining Unit, Indian Refining Company, Lawrenceville, Ill. (Looking southeast).

in vaporizing at atmospheric pressure about 50 percent of the solvent in the extract mixture. The vapor from this operation is used to heat and evaporate most of the remaining furfural in the bottoms under vacuum, in the second stage. Circulation through the heater effects the evaporation of all but the final trace of solvent. Extract from the circulation is bled to a vacuum steam stripper, where about 0.4 to 0.5 percent by weight of furfural is removed. The vapors from this steam stripper are condensed together with vapors from the refined oil stripper, and the combined condensates pumped to slop solvent. Dry solvent from the extract vacuum stripper, together with dry solvent from the refined oil stripper, is condensed in a common condenser, and transferred from the receiver to the recovered solvent tank for use in extracting more oil.

Slop solvent is pumped to a separate tank from which the slop solvent pump transfers the furfural layer through the solvent drier and the water layer to the fractionator. The fractionator consists of three separate sections—the stripping section, the fractionating section, and the separating section. Steam is introduced to the bottom of the stripping section, and all vapors are condensed at the top and returned to the separating section—where wet furfural layer is continuously removed through a cooler and external separator. Furfural-saturated water is continuously returned to the separating section, while water-saturated furfural is run to the solvent drier. The design and operation of this type of solvent fractionator were described by Mains.[3]

The solvent drier is a simple device in which wet solvent is heated to 310°F. for removal of water. Water vapor and furfural vapor return to the fractionator, while dry liquid furfural is run to the dry solvent accumulator for re-use.

SOLVENT LOSSES

Due to the fact that furfural goes off color when handled in open laboratory equipment, question has arisen concerning its stability. A careful investigation of this subject in the laboratory prior to the plant construction demonstrated that the actual amount of furfural involved in the color reaction was minute, and that solvent losses in a properly designed plant should be well within the economic limit. This conclusion has been definitely substantiated in plant operation.

In a closed system in plant operation the solvent

TABLE 1

Average Furfural Losses

(Plant Operating Data)

PERIOD	Total Barrels Oil Treated	Total Barrels Furfural Used	Gallons Furfural Loss	Percent Furfural Loss (Basis Furfural Used)	Gallons Furfural Lost Per Barrel of Oil Charged
3-31-34 to 6-4-34...	79,873	152,765	3,243	0.0505	0.0406
6-4-34 to 8-14-34...	84,228	159,612	2,889	0.0431	0.0343
8-14-34 to 11-12-34.	100.753	212,420	2,251	0.0252	0.0223
Total for period 3-31-34 to 11-12-34.	264,854	524,797	8,383	0.0380	0.0316

remains a very light yellow color, and plant losses have been very low—even though recovery temperatures as high as 600°F. have occasionally been reached. Table 1 gives solvent losses in plant operation as determined by actual inventories over an eight months operating period. It will be noted that the losses have gradually decreased as line leakage and other defects inherent in a new plant have been corrected. During the initial stages of operation, contamination of the solvent with water from a broken condenser tube and other operating difficulties made initial losses rather high. Correction of these difficulties has reduced the solvent loss to only 0.025 percent of the total furfural used, as determined by plant inventory over the operating period of August 14 to November 12, 1934.

In the Lawrenceville plant the solvent is recovered approximately eight times in each 24 hours of operation. Recovered solvent is of better quality than new solvent due to decreased organic acidity and improved color. Recovered furfural is tested daily for moisture content and percent of oil. Moisture is kept below one percent by weight.

INVESTMENT AND OPERATING COSTS

Furfural refining plant installation costs are dependent to a large extent on each refiner's individual problem. In general, the initial investment for furfural refining is relatively low, ranging from about $300 per barrel of daily charge capacity for units of 500 barrels per day capacity to about $70 per barrel of daily charge capacity for units having a daily charge rate of 5000 barrels per day.

Due to the relatively simple extraction tower, investment costs are lower than would be the case where step-counter-flow equipment is required. Plant design is likewise adapted to the efficient utilization of recovered refinery equipment.

In Table 2 are presented the labor requirements, utilities requirements, and average operating conditions of a commercial furfural refining unit having a nominal capacity of 1350 barrels of Mid-Continent distillate (all grades) per day.

Labor requirements are based on actual operating conditions at the Lawrenceville plant, where the operating foreman and shift foreman handle other operations in addition to the furfural refining unit. The labor requirements are sufficient to take care of a much larger unit, and unit labor costs on a larger plant would be reduced practically in proportion to the production.

In the Lawrenceville plant all pumps are steam-driven, exhaust steam being credited for use in other parts of the refinery. Due to the use of steam, electric power costs are low. A circulating water system with a cooling tower is in use which reduces the water requirements to evaporation and mechanical loss requirements.

The average operating conditions are those in use at Lawrenceville, but do not necessarily represent the optimum conditions for a Mid-Continent distillate. Production requirements, which have forced operations well above rated capacity, have necessitated changes in operating conditions from what would be used under normal conditions.

TABLE 2

Furfural Refining Unit

Labor Requirements:

Labor	Hours	Hourly Rate	Daily Cost
Operating foreman	4	$1.50	$6.00
Shift foreman	8	1.25	10.00
Operator	24	0.90	21.60
Helper	24	0.75	18.00
Laborer	3	0.55	1.65
Total			$57.25

Utilities Requirements:

Fuel.....0.0443 bbl. of fuel per barrel of charge.
Steam.....151 lb. per barrel of charge.
Water pumping.....0.943 kwh. per barrel of charge.

Average Operating Conditions—Wax Distillate No. 40.

Stock:	
Oil charged to plant, °F	120
Temperature of oil charged to counter-flow tower, °F	195
Temperature of furfural charged to counter-flow tower, °F	255
Temperature top of tower, °F	235
Temperature bottom of tower, °F	200
Ratio of furfural to oil charged by volume	1.97 to 1
Fuel distribution: Extract, percent	77.02
Raffinate, percent	22.98
Plant charge rate (42-gal. barrels), bbl. per day	1,330
Furfural loss (average), percent of furfural used	0.0380

Table 3 gives a detailed statement of operating costs for a typical operating month. Total direct operating expense amounts to only $0.1739 per 42-gallon barrel of charge.

TABLE 3

Operating Costs—Furfural Refining Unit

(Exclusive of Royalties)

	Unit Cost (Basis Barrels of Charge)	
Operating labor	$0.0366	
Material, supplies, and others	0.0033	
Fuel	0.0496	
Steam, power, and water	0.0493	
Total operating		$0.1388
Repair labor	0.0020	
Material, supplies, and others	0.0026	
Total repairs		0.0046
Furfural loss		0.0305
Total direct expense, per barrel		$0.1739

It is felt that the low operating costs are quite satisfactory; and, in the case of the Lawrenceville installation, have resulted in a finished solvent refined oil at a lower direct cost than when the oil was acid-treated only without the use of solvent. This decrease in cost has resulted in part from generally improved and simplified processing operations and from the increased value of extract over acid sludge.

TESTS ON FURFURAL REFINED OILS

In Table 4 is presented a tabulation illustrating the tests on the raw lubricating stocks, together with the results obtained in the furfural refining plant operations. Tests also are shown on the same oils dewaxed by the acetone-benzol process.

Attention is called to the fact that this plant is operating at present in the production of oils having viscosity indices and other characteristics which are

TABLE 4
Furfural Refining Mid-Continent Distillates

	Light Mid-Continent Distillate				Heavy Mid-Continent Distillate				Extra-heavy Mid-Continent Distillate			
Dosage furfural in, per cent by volume	191				190				191			
Temperature tower top, ° F.	200				235				240			
Temperature tower bottom, ° F.	170				212				220			
Yield raffinate, per cent by volume	77.0				72.5				66.5			
Yield extract, per cent by volume	23.0				27.5				33.5			
INSPECTION	**Raw Charge**	**Raffinate**	**Extract**	*** Wax-free Product**	**Raw Charge**	**Raffinate**	**Extract**	*** Wax-free Product**	**Raw Charge**	**Raffinate**	**Extract**	*** Wax-free Product**
Gravity, API	25.6	30.8	11.2	28.6	23.1	28.6	10.7	26.5	20.8	27.1	10.3	26.2
Flash point, Cleveland open cup, ° F.	440	450	...	450	500	510	...	505	550	550	...	555
Fire point, Cleveland open cup, ° F.	510	510	...	510	580	575	...	580	625	625	...	630
Viscosity at 100° F., Saybolt Universal	...	...	...	298	1,300	650	...	932	5,000	1,220	...	1,697
Viscosity at 130° F., Saybolt Universal	141	110	...	...	...	281	...	...	...	...	...	635
Viscosity at 210° F., Saybolt Universal	50	48	81	52	87	72	247	82	176	102	70 Furol	112
Carbon residue, percent	0.27	0.03	...	0.04	1.40	0.14	...	0.25	3.70	0.40	...	0.35
Color	...	...	Black	100 (6″ cell) Lovibond	...	...	...	40 (½″ cell) Lovibond	Black	...	...	3 Tag.
Pour point (ASTM), ° F.	50	100	...	—5	110	115	...	—5	+80	120	...	—5
Viscosity index	72.5	105	...	95	64	97	...	87	54	97	...	85

* Oils are finished with three to seven pounds of acid per barrel contact-filtered and dewaxed by acetone-benzol process.

TABLE 5
Furfural Refining for High Viscosity Index
(Pilot Unit Operation)

Solvent dosage, percent by volume	292
Top-tower temperature, ° F.	243
Bottom-tower temperature, ° F.	229
Yield, percent raffinate by volume	51.3

INSPECTION	Raw Charge	Raffinate	Extract	* Treated Raffinate
Gravity, API	21.3	29.4	13.1	29.6
Flash point, Cleveland open cup, ° F.	465	480	...	500
Fire point, Cleveland open cup, ° F.	555	570	...	565
Viscosity at 100° F., Saybolt Universal	...	520	...	500
Viscosity at 130° F., Saybolt Universal	444	235	483—160	233
Viscosity at 210° F., Saybolt Universal	80.5	65	128	66
Pour point (ASTM), ° F.	—10	—5	...	—5
Color	½ Tag	30 (½″ cell) Lovibond	Black	15 (6″ cell) Lovibond
Carbon residue, percent	0.69	0.03	1.90	0.02
Viscosity index	53	98	...	103
Viscosity-gravity constant	0.862	0.801	...	0.802

* Finishing treat, five pounds 98 percent acid per barrel, contact-filtered with seven pounds of clay.

considered at present to be satisfactorily high for superior performance in service. Increase in solvent dosage and modification of operating conditions would result in higher viscosity indices. It is noted that the viscosity index of the low viscosity oil insures easy starting in cold weather; while the oxidation tests in Table 7, on both light and heavy oils, indicate their exceptional resistance to sludging and other deterioration characteristics of high-temperature operations. It is noted that the yields obtained are particularly high due to the degree of selectivity of furfural as a refining solvent. A further sacrifice in yields and increased cost of operation is not considered justified at present for the doubtful advantage of a few points increase in viscosity index.[5]

The finishing steps employed in manufacture of low pour test solvent-refined lubricants consist in acid-treating raffinate with two to five pounds per barrel of 98 percent acid, contact neutralizing with four to 12 pounds per barrel of contact clay, and dewaxing with acetone-benzol to a pour test below 0°F. The light acid treatment is considered more efficient and economical than straight percolation or contact filtering, although a satisfactory product can be made by the latter methods using no acid.

Road tests conducted on furfural refined oils have confirmed the laboratory tests made on these oils; and in service the furfural refined oils show much less carbon deposition and sludge formation, with slightly less consumption, and less change of viscosity in service, than high viscosity index oils which have not been refined by solvent means.

The ability of the furfural refining process to produce oils having a viscosity index of above 100 has

TABLE 6
Oxidation Tests, Furfural Refined Oils

	Furfural-refined No. 20	Furfural-refined No. 40
Gravity, API	29.1	27.9
Flash point, Cleveland open cup, °F.	435	490
Fire point, Cleveland open cup, °F.	495	560
Viscosity at 100° F., Saybolt Universal	317	716
Viscosity at 210° F., Saybolt Universal	52.5	72
Viscosity index	89	87
Pour point, °F.	—5	—5
Carbon residue, percent	0.04	0.12
Sligh oxidation No.	0.5	0.80
B. E. S. A. sludge	0.09	0.04
German method tar-forming No.	0.06	0.04
Appearance of heated oil after cooling	Clear transparent red oil	Clear transparent red oil
Sludge insoluble in benzine	None	None
Separation of sludge after heating with sodium hydrate	None	None
Standard Oil Company (Indiana) oxidation test[4]		
Hours for 10 mg. sludge per 10 g.	68	105
Hours for 100 mg. sludge per 10 g.	124	153
Test period, hours	166	166
Viscosity at 210° F., Saybolt Universal, after period	65	95

TABLE 7
Pilot-Unit Runs of Typical Stocks

OIL SOURCE	Pennsylvania Steam-refined Residuum			
Percent furfural by volume		276		
Temperature top tower, ° F		249		
Temperature bottom tower, ° F		232		
Percent raffinate by volume		84.2		
Percent extract by volume		15.8		
	Charge	Refined Oil	Extract	Contacted Refined Oil 35 Lb. Filtrol Per Barrel
Gravity, API	25.1	27.8	12.1	28.2
Flash point, Cleveland open cup, ° F	560	550	...	560
Fire point, Cleveland open cup, ° F	640	640	...	635
Viscosity at 100° F., Saybolt Universal	...	1,790	...	1,900
Viscosity at 130° F., Saybolt Universal	955	750	...	770
Viscosity at 210° F., Saybolt Universal	162	147	...	142
Pour point, ° F	35	...	...	45
Carbon residue, percent	3.06	1.41	...	1.14
Color	Black	Dark green	...	¾ Tag-Robinson
Viscosity index	...	113	...	107
Viscosity-gravity constant	...	0.799	...	0.797

OIL SOURCE	Pennsylvania Neutral				Gulf Coastal Distillate			
Percent furfural by volume	197				206			
Temperature top tower, ° F	200				195			
Temperature bottom tower, ° F	172				175			
Percent raffinate by volume	86.0				63.3			
Percent extract by volume	14.0				36.7			
	Charge	Refined Oil	Extract	Refined Oil Dewaxed	Charge	Refined Oil	Extract	Refined Oil, Contact-filtered
Gravity, API	30.8	33.5	16.7	32.2	18.8	24.0	10.6	24.0
Flash point, Cleveland open cup, ° F	420	420	420	425	480	450	460	475
Fire point, Cleveland open cup, ° F	475	470	475	480	535	525	525	535
Viscosity at 100° F., Saybolt Universal	152	136	705	159	1,810	950	...	915
Viscosity at 210° F., Saybolt Universal	44	44	58.5	45	82	70	152	70.5
Pour point, ° F	75	70	50	0	—5	0	...	—5
Carbon residue, percent	0.06	0.02	0.90	0.02	0.14	0.04	1.10	0.04
Color	...	...	...	200 (6″ cell) Lovibond	4¾ Tag-Robinson	...	Black ...	120 (6″ cell) Lovibond
Viscosity index	104	123	+11	111	—3.5	...	...	52
Viscosity-gravity constant	0.818	0.803	...	0.808	0.881	...	...	0.844
Steam emulsion No	...	...	...	...	...	...	...	90
Demulsibility	...	...	...	...	...	...	...	1,620
Navy emulsion:								
Water	...	...	...	...	...	...	...	40-40-0- 4
Brine	...	...	...	...	...	...	...	40-40-0-15
Caustic	...	...	...	...	...	...	...	40-40-0-15

been clearly demonstrated in pilot unit counter-flow-tower runs. In Table 5 are shown data on the furfural refining of a wax-free heavy distillate stock dewaxed in the raw state prior to furfural refining. In furfural treatment of dewaxed 180 viscosity (at 100°F.) pale oil from Pennsylvania stocks, viscosity indices of 120 (Dean and Davis) have been obtained with excellent yields of product.

APPLICATION OF FURFURAL TO VARIOUS LUBRICATING STOCKS

Although the furfural refining plant at Lawrenceville has operated on Mid-Continent distillates only, many pilot unit runs have clearly established the application of furfural to a very wide variety of lubricating stocks. In Table 8 are shown the results of pilot unit runs in refining the following typical stocks:

1. Pennsylvania neutral
2. Pennsylvania residuum
3. Coastal distillate.

The results shown in Table 7 on Pennsylvania residuum indicate the removal of undesirable constituents with good yields of refined oil. The action of furfural on steam-refined Pennsylvania stock renders this stock much more susceptible to clay filtration to a given color specification, and lowers the carbon residue.

On the Pennsylvania neutral oil, high yields of refined oil are obtained with a considerable improvement in viscosity index and carbon residue.

On Gulf Coast distillate reasonably high yields of high quality refined oil are noted. Without acid treatment the viscosity index has been increased 55 points, and with only a light clay-contact treatment the product has excellent demulsibility tests.

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Laboratory Distilling Apparatus

(*Continued from page 282*)

at 2 mm. For reduction to higher viscosity, more satisfactory results are obtained by the use of a small amount of steam. When steam is used, it is necessary to connect the jet-condenser system of the flash vacuum unit into the vacuum line between the distillate receiver and the vacuum pump. Permanent connections have been made for this purpose so that the change from dry to wet vacuum can be made by manipulation of three valves.

In order to determine the relative fractionating efficiency of this unit, a proportionate blend of the distillates from a commercial vacuum unit was made as follows:

	(Percent)
Vacuum gas oil	15.9
Light wax distillate	44.2
Heavy wax distillate	17.6
Overhead cylinder stock	22.3

The above blend was distilled in the laboratory unit—taking overhead the gas oil, light wax distillate, and heavy wax distillate, and leaving the cylinder stock as bottoms. Table 5 gives a comparison of the assay distillations, gravities, and yields of the products obtained with those of the original oils before blending. It will be noticed that closer cut fractions are obtained from the laboratory unit than from the commercial unit. The greater sharpness of the cut between heavy wax distillate and cylinder stock is particularly noticeable.

CONCLUSION

While no claims for originality are made, it is believed that each of the four distilling units described in this paper embody features which may be of interest to others engaged in this type of work. With the exception of the pumps and motors, the entire equipment can be constructed at reasonable cost in any refinery equipped with a machine shop and welding facilities. Although the units were designed primarily for crude oil evaluation, each one has been used for a variety of purposes in connection with research and development problems.

Additional equipment has also been constructed for treating, dewaxing, and contacting lubricants so that the various distillation products may be refined to finished products in quantities sufficient for all analyses and tests necessary to determine their quality.

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Fuel Specifications for High-Speed Diesel Engines

(*Continued from page 241*)

the Diesel engine just as tetra-ethyl lead is used to prevent detonation in the gasoline engine. Hubner and Murphy state that the use of the known fuel dopes will be restricted because:

1. Ethyl nitrate and amyl nitrate are too expensive.
2. Acetaldehyde is too volatile.
3. Benzaldehyde decomposes too rapidly.

POSSIBILITIES OF IMPROVING FUEL

The refiner has the broad possibilities of taking a cracked distillate, or whatever may be left over from the refining of the more valuable products such as gasoline, and making it into a good Diesel fuel. It may require some chemical changes; and in order better to understand the fuel, it will require careful combustion studies. The difference between rough and smooth operation is a matter of what happens in the combustion chamber during the few thousandths of a second after the beginning of fuel injection.

Combustion in the Diesel engine is commonly considered as taking place in three states: First, a delay period—during which fuel is being injected, but no pressure rise occurs due to combustion. Second, the pressure rises rapidly out of control. The greater the delay period, the more severe will be the shock due to this rapid pressure rise. Third, the remainder of the fuel is injected and burned under control. Mr. Rose of the University of Wisconsin has developed an indicator which permits a detail study of these periods. He has found it possible to sub-divide the period of the first phase of combustion into two distinct periods, by determining the point at which combustion actually begins. One of the greatest needs at the present time is better correlation of laboratory information on Diesel fuels with service tests in the field.

Analytical Solvent Fractionation of Lubricating Oils

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BY suitable choice of conditions in solvent extraction by the multiple-batch method, an analytical procedure has been developed for solvent fractionation of oils in the lubricating oil range. This procedure makes it possible to separate an oil into a series of cuts of varying paraffinicity. The results, conveniently shown as composition curves, permit close estimation of possible yields of oil of specified quality or give valuable information on the composition of finished motor oils.

Examination of various stocks has shown that the differences between them are much more in the relative proportion of the different constituents present than in the constituents themselves. By the analytical fractionation procedure developed, it is possible to determine whether any particular stock contains a sufficient proportion of oil of specified quality to make production of such oil economically feasible.

Solvent fractionation of finished motor oils shows the extent to which the low grade components have been eliminated in the refining operations. Data on a large number of typical motor oils show a wide variation in this respect, but the absence of the low grade low API-gravity constituents in highly refined solvent-extracted oils is very noticeable. Because of the adverse effects of such constituents on quality, the analytical results are valuable in predicting the performance to be expected in service.

This paper was presented at Fifth Mid-Year Meeting, American Petroleum Institute, Tulsa, May 16, 1935.

IT IS well recognized that lubricating oils obtained from petroleum are complex in composition, and that the usual physical and chemical tests give average values for the oil as a whole, rather than information on its range of composition. Distillation, followed by application of the usual tests to the respective cuts, extends our knowledge of the composition of the oil; but at best this type of segregation of the oil into component fractions effects a grouping of the components only as regards boiling points or molecular weights, and fails to give a clear picture of the chemical make-up of the oil.

The use of solvents to effect a separation of hydrocarbon oils into components of varying chemical types has been studied by many investigators[1 2 3] during the last 30 years, and the literature on solvent extraction is now quite voluminous. The work of the earlier investigators was not particularly successful, largely because of using unsuitable solvents and applying them to stocks of excessive boiling range. In the last few years attention has been directed principally toward the development of solvent refining processes, but the need is still felt for an analytical method of separating and classifying the components of a lubricating oil according to chemical structure. During the course of experimentation on solvent extraction in the laboratories of Union Oil Company, a routine analytical procedure has been developed for the multiple-batch method of extraction. The purpose of this paper is to present this procedure and to show that reproducible and informative composition curves for lubricating oils can be obtained by the choice of conditions of extraction in accordance with definite principles.

In a study of the factors influencing fractionation in solvent extraction, the analogy to the more familiar fractionation by distillation is helpful. This analogy has doubtless been recognized for some time by investigators in this field, and has recently been discussed in some detail by Saal and Van Dyck[4]; so that it is sufficient to point out the similar function of the solvent in a solvent extraction operation and the steam in the usual steam distillation in which no liquid water is present in the still. It is frequently the practice in steam distillation in a batch still to adjust the still temperature as the distillation progresses, so that the oil and water are recovered overhead in a constant ratio. Under such conditions the still or vapor temperature plotted against the percentage of oil distilled will follow a definite and reproducible curve for any given stock. Similarly, in analytical solvent extraction, it is desirable to maintain a substantially constant concentration of oil in the extract phase. This is readily accomplished by raising the temperature between one batch extraction and the next. If a constant volume of solvent is used for each extraction, and the concentration of oil dissolved in the solvent is maintained approximately constant, cuts of uniform size will be obtained. In solvent fractionation, separation is accomplished through differences in solubility. These differences are due principally to variation in chemical composition in a mixture of compounds of about the same molecular weight. It is apparent that, just as in a steam distillation cuts of successively higher molecular weight are obtained by progressively raising the temperature, so in solvent extraction cuts of increasing paraffinicity may be obtained by starting the series of extractions at a low temperature and progressively working upwards.

For the sake of convenience in the absence of strict knowledge regarding the molecular configuration of each hydrocarbon compound present, we may follow

the change in chemical structure by the change in some property dependent on molecular composition, such as gravity, viscosity, or refractive index for a given molecular weight (or, more strictly, number of carbon atoms in the molecule). When successive extract fractions are subjected to inspection tests and the respective values are plotted against the total amount of material removed up to the mid-point of the cut in question, composition curves are obtained which are analogous to an ordinary Engler distillation curve. It will be recalled that the Engler distillation approximates a simple distillation without rectification, in that at any instant the vapor is in equilibrium with the liquid remaining in the still; and, therefore—theoretically at least—the vapor will contain some small proportion of all of the components remaining in the still. Similarly, in the batch method of extraction, the extract phase is in equilibrium with the raffinate remaining, and theoretically contains some small proportion at least of all the components of the raffinate. However, just as in practice the degree of fractionation obtained in the usual Engler or batch steam distillation without rectification is adequate for many purposes, likewise the fractionation obtainable in multiple-batch extraction is valuable in giving composition curves.

In simple distillation the differences in vapor pressure of the components can be accentuated, and the fractionation consequently improved—through operation at a lower temperature under reduced pressure or with a carrier gas, such as steam. Similarly, in solvent extraction the differences in solubility of the components in the solvent can be accentuated and the efficiency of separation improved by operating at the lowest temperature consistent with a reasonable yield of extract for each batch of solvent. Fundamentally, the two most important principles in analytical solvent extraction by the multiple-batch method are: 1, operation at temperatures increased at such a rate as to give constant oil concentration in the successive extract phases; and, 2, choice of temperatures in general sufficiently low as to restrict the oil concentration in the extract phase to a reasonably small value. With proper attention to these principles and to certain operating details, the fractionation obtained permits analysis of practically all classes of lubricating oils. Some of the more important applications are as follows:

1. Analysis of lubricating stocks to estimate the available yield of oils of various qualities.
2. Analysis of extract oils produced as by-products in solvent refining to estimate the loss of high-grade oil in the refining operation.
3. Analysis of finished lubricating oils to determine the composition of oils offered for use or being used as lubricants, and as a control on the refining process.

The procedure to be used for each of these groups will be described separately, but it is believed advisable to point out first certain essentials which the operator should follow with all classes of oils.

PRECAUTIONS TO BE OBSERVED IN ANALYTICAL SOLVENT EXTRACTION

In order to obtain the most reliable data, the following precautions should be observed:

1. Choose the temperature and volume of solvent for each batch extraction to give a maximum of four to six percent oil concentration by volume in the extract phase.
2. Allow sufficient time of agitation at extraction temperature to guarantee equilibrium between phases.
3. Allow ample time of settling at extraction temperature to give complete separation of phases, and carefully avoid drawing any of the raffinate phase with the extract phase.

Because of its influence on the selectivity of the solvent, too much emphasis cannot be placed on the necessity of restricting the concentration of dissolved material in the extract phase. The ideal solvent will have infinite solvent power for materials below a certain gravity or viscosity index, and practically no solvent power for materials of higher gravity or viscosity index—with the point of differentiation or cutting dependent upon the temperature. Even with this ideal solvent, it is probable that the presence of any appreciable amount of extract dissolved in the solvent would impair the selectivity because of the extract being a common solvent for the extracting agent and the high grade components of the stock. Theoretically, therefore, the greatest selectivity is obtained with the pure solvent; and to preserve this selectivity, the concentration of dissolved material should be kept at a minimum. For practical purposes, however, several percent of dissolved material can be tolerated in the extract, with the tolerance depending upon the particular selective solvent. Obviously, successive cuts of any desired size can be obtained without exceeding the desired concentration in the extract phase—by using sufficient solvent and restricting the temperature. For any particular solvent the temperature required will be influenced by the desired cutting point, and the actual proportion of the stock existing below this cutting point. For example, aniline may be used efficiently at approximately 100° F. to remove fractions having gravities in the range of about 15 to 20 degrees A. P. I., whereas the chloroanilines require a temperature in the neighborhood of 50° F. to accomplish approximately the same result.

Also, certain solvents such as phenol, chloroaniline, and nitrobenzene can tolerate, without losing appreciable selectivity, a higher percentage of extract than other solvents, such as Chlorex, sulfur-dioxide—benzene, furfural, and aniline. The solvents shown in the first group, however, have high solvent power for low-gravity components of lubricating stock, even at temperatures approaching their freezing points. In consequence, their solvent power cannot be sufficiently reduced by lowering the temperature, and they are not well suited to give a complete analysis of lubricating stocks or finished oils containing considerable amounts of low grade materials. Phenol, for example, may be used satisfactorily in segregating lubricating materials of better than 20 degrees A. P. I. gravity, but it is unsuited for separating materials of lower gravity. Either aniline or Chlorex, however, can be used conveniently and satisfactorily over the entire range of gravities or viscosity-gravity constants encountered in an untreated lubricating stock.

With either aniline or Chlorex, the limit of oil tolerance in the extract phase consistent with the best practical analytical results is apparently less than eight percent by volume, and the concentration is preferably held at less than six percent by volume.

Chlorex has the advantages over aniline of causing less charring or polymerization of low gravity extracts during topping to remove solvent, and producing a greater reduction in viscosity during the extraction, as well as having lower toxicity. With reasonable care, the objection to aniline in these respects is not serious, and the choice between aniline and Chlorex for conducting analytical extractions is believed to be mainly a matter of convenience.

In applying each dump of solvent, mechanical agitation for 15 to 20 minutes after reaching the chosen temperature is adequate to insure equilibrium. Violent agitation sufficient to cause emulsification appears to be unnecessary and, in fact, is less desirable than more gentle agitation on account of the danger of failing to secure complete separation of the raffinate out of the extract phase after emulsification. During the period of agitation and settling the temperature is generally held constant to within 2 or 3° F. Closer temperature control is probably unnecessary.

Adequate time of settling to obtain complete separation of phases is extremely important. Both phases should be well settled, particularly the extract—which should be transparent, and not murky. The existence of even a small concentration of emulsified raffinate or stock in the voluminous extract phase will have the two-fold ill effect of giving unduly high gravities for the contaminated extracts and a lower yield of high-gravity components subsequently. As a precaution, even though the lime of demarcation between the phases is very sharp, it is believed that no attempt should be made to withdraw the last trace of extract phase. With Chlorex, a settling time of about one hour at the lowest temperatures required on a medium-viscosity lubricating distillate is generally adequate, although a more viscous stock will require a longer time.

ANALYSIS OF LUBRICATING STOCKS

The analysis of a lubricating stock can be carried far enough to give a complete composition curve, or only sufficiently to give yields of oil of specification quality remaining as the raffinate. The gravity of the raffinate at any point may be calculated arithmetically from the gravities of the stock and extract fractions in conjunction with the respective extract-yield figures, and verified by actual tests on the raffinate or on re-composites of raffinate and the proper extracts in case the raffinate has been carried beyond specification quality.

To obtain the most reliable composition curve for untreated lubricating stocks using Chlorex as the solvent, it is recommended that the solvent be applied in dumps of 200 volume percent, and that the extractions be started at approximately 0° F., and the temperature raised at a maximum rate of 10° F. between consecutive dumps. When the character of the material removed is changing only slowly, more than one dump can often be applied advantageously before raising the temperature. The temperatures at which the multiple extractions are performed may be varied with the average molecular weight or viscosity grade of stock during the later extractions. Using either aniline or Chlorex, an SAE-50 stock may be extracted at 25 or 30° F. higher temperature during the latter part of the fractionation than an SAE-20 stock.

As an example of the procedure employed and the results obtained, the data shown in Table 1, and reproduced graphically in Figure 1, are taken from the complete fractionation with Chlorex of a dewaxed Santa Fe Springs lubricating distillate which produces normally an SAE-20 raffinate. Curve 1 represents a plot of the gravity-yield data shown in the table. It is of interest to point out that the yield of raffinate of 30.0 A. P. I. gravity, corresponding

TABLE 1

Analytical Solvent Fractionation of Propane-dewaxed Santa Fe Springs SAE-20 Distillate

SAMPLE	Solvent Chlorex (Volume Percent)	Temperature of Extraction (°F.)	Recovery (Volume Percent)	API Gravity at 60° F.	Pour Point (°F.)	Viscosity, Saybolt Universal Seconds, at: 100° F.	Viscosity, Saybolt Universal Seconds, at: 210° F.	Viscosity Index	Viscosity-Gravity Constant
NORMAL METHOD									
SAE-20 stock	...	...	...	20.3	0	760	63.5	33	0.874+
Extract 1	250	—5	24.61	6.1	..	...	200	..	0.979
Extract 2	200	5	8.45	10.7	..	...	112	..	0.945
Extract 3	200	12	5.73	15.8	..	...	74.5	..	0.908
Extract 4	200	18	4.14	18.6	..	...	65.5	..	0.888
Extract 5	200	17	4.11	21.1	..	...	61.5	..	0.869
Extract 6	200	23	3.54	22.4	..	...	58.5	..	0.860
Raffinate 6[a]	...	..	49.43[b]	30.0	..	307.9	52.4	94	0.807
Extract 7	200	32	3.47	23.9	..	...	57.5	..	0.849
Extract 8	200	41	3.76	25.0	..	...	57.0	..	0.841
Extract 9	200	42	3.40	26.0	..	...	55.5	..	0.834
Extract 10	200	49	4.10	27.3	..	...	55.0	..	0.825
Extract 11	200	50	3.50	28.1	..	...	55.0	..	0.819
Extract 12	200	50	3.35	28.8	..	...	54.0	..	0.814
Extract 13	200	50	3.08	29.4	..	...	55.0	..	0.809
Extract 14	200	50	2.74	30.0	..	...	54.5	..	0.805
Raffinate 14	...	...	22.02[b] 19.27[c]	33.6	20	235.1	50.0	113	0.784
Total	2,850								
SHORT METHOD									
SAE-20 stock	...	...	...	20.3	0	760	63.5	33	0.874+
Extract 1	250	49	35.82	10.9	..	...	110	..	0.944
Extract 2	250	60	14.67	17.8	..	...	66	..	0.894
Extract 3	250	70	10.63	22.7	..	...	58	..	0.858
Extract 4	250	86	11.13	26.4	..	...	56	..	0.831
Extract 5	250	101	12.76	29.5	..	...	54	..	0.809
Raffinate	...	...	14.99[b] 14.10[c]	32.4	—5	276	52.3	108	0.790
Total	1,250								

[a]Raffinate 6 was prepared synthetically at the end of the run by blending extracts 7 to 14, inclusive, with raffinate 14.
[b]Percentage by difference.
[c]Percentage from actual recovery of topped raffinate.

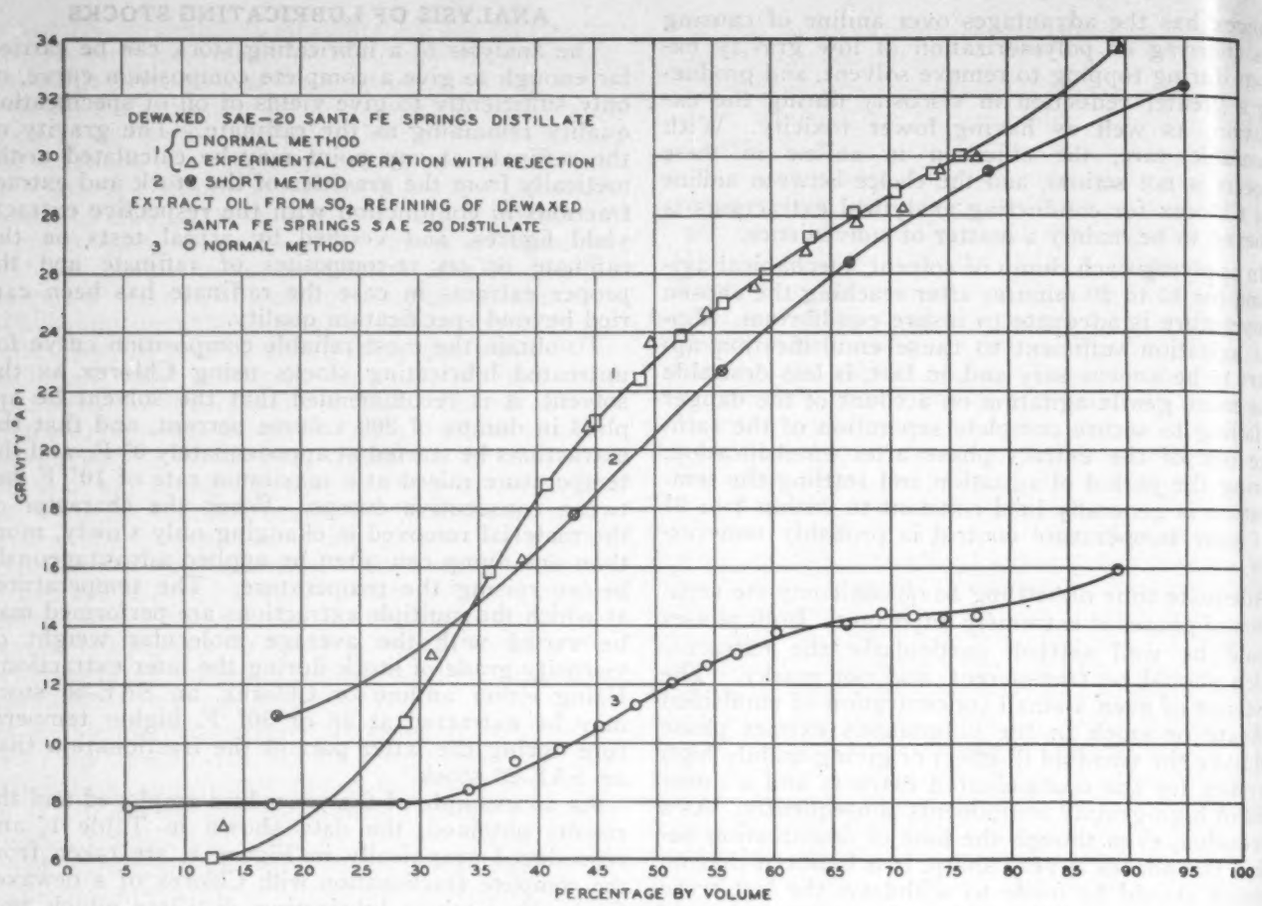
DEWAXED SAE—20 SANTA FE SPRINGS DISTILLATE
1 □ NORMAL METHOD
△ EXPERIMENTAL OPERATION WITH REJECTION
2 ● SHORT METHOD
EXTRACT OIL FROM SO_2 REFINING OF DEWAXED SANTA FE SPRINGS SAE 20 DISTILLATE
3 ○ NORMAL METHOD
GRAVITY °API
PERCENTAGE BY VOLUME
1
2
3

FIGURE 1
Solvent Fractionation of Lubricating Stock.

in this case to a viscosity-gravity constant of 0.807, was calculated to be 49.5 percent on the basis of the gravity of the stock and the extract-gravity curve, and that this calculated yield was later checked within one percent by compositing the final raffinate and extracts until a gravity of 30.0 A. P. I. was obtained. To illustrate the reliability of this figure, it may be stated that this stock gave within one or two percent of the same yield of specification oil of 0.807 viscosity-gravity constant when subjected to efficient continuous counter-current extraction with sulfur dioxide—benzene in 12 stages. It is interesting to note that although two different solvents were used—the one for analytical fractionation of the stock and the other for refining the stock—the results are in agreement.

Consideration has been given to the possibility of improving the results of the foregoing method of analytical fractionation of lubricating stocks by combining a rejection step with each extraction. Instead of performing the extraction with a given dump of solvent at a specified temperature by simply mixing, settling, and separating the phases as just described, the same amount of solvent is agitated with the stock, or raffinate from a previous extraction, at a temperature considerably higher than that chosen for the final separation of the extract phase; the agitated mixture is allowed to settle at this higher temperature; and the extract phase is withdrawn and cooled to the same temperature as used in the corresponding direct extraction. The cooled extract is then agitated sufficiently to insure equilibrium between the extract phase and any oil rejected at the lower temperature. After the mixture has settled thoroughly, the extract phase is withdrawn for distillation to recover solvent and the extract cut, and the rejected oil is returned to the raffinate. Theoretically, the final extract obtained in this manner should contain less high grade oil than the extract obtained in the direct manner at the same final temperature—on account of the fact that the final extract phase obtained in the rejection procedure is not in equilibrium with the raffinite phase remaining from the original stock, but is in equilibrium with the rejected-oil phase which should contain a lower percentage of high grade components. Adding the rejection feature to the extraction procedure described above obviously increases the time and labor required to complete the solvent fractionation, and it was considered desirable to evaluate the practical advantages of the additional effort. Fortunately, from the standpoint of obtaining useful information by the direct-extraction method, the theoretical advantages of the rejection step were not realized in practice. An analytical extraction, paralleling as closely as possible the experiment shown in Table 1, was performed—except that the additional feature of temperature rejection was employed as indicated. The results of this experiment are shown graphically in Figure 1 as points only, since they fall practically on curve 1 for the direct extraction method. Any differences shown are considered not significant, as they are no more than could be caused by experimental error. The foregoing experience with rejection as applied to multiple-batch extraction does not necessarily mean that some form of temperature

rejection cannot be used advantageously in continuous counter-current extraction.

To conserve time and expense, less efficient fractionation is often permissible—especially after sufficient experience is obtained to permit an approximate correction for the loss of efficiency in fractionation. Such a fractionation is obtained, for instance, by applying four or five 250-volume-percent dumps of Chlorex or aniline at temperatures ranging progressively from 50 to 100° F. for an SAE-20 stock. Such an extraction was performed on the same stock as in the previous experiments, and the data obtained are shown in Table 1. In this case the extracts are contaminated with appreciable amounts of the higher grade materials, giving a less steep curve displaced to the right when plotted as in curve 2 of Figure 1.

ANALYSIS OF BY-PRODUCT EXTRACT OILS

The fractionation of by-product extract oils is conducted much the same as with a lubricating stock, except that with extract oils larger solvent ratios and lower temperatures are usually required during the first part of the extractions. As would be expected, it is somewhat more difficult to restrict the concentration of dissolved material in the extract phase; but, by using more solvent at lower temperatures, acceptable results can be obtained. With an extract oil from an untreated SAE-20 lubricating distillate, for example, the extraction should be started with a 450-volume-percent dump of Chlorex at a temperature of —15° F. Curve 3 of Figure 1 represents the analysis of a sulfur-dioxide extract from dewaxed SAE-20 distillate.

ANALYSIS OF FINISHED MOTOR OILS

The analysis of finished motor oils may be for the purpose of determining the amount and character of the lowest grade components present or to obtain a complete composition curve. Since most finished motor oils, particularly those of higher quality, will show only a small content of low gravity oil, it is generally permissible to begin the analysis of a finished oil at a temperature in the neighborhood of 100° F. using aniline, or 50° F. using Chlorex. Because of the greater uniformity of finished oils as compared to raw stocks, a routine procedure of analysis is possible. A recommended schedule of extractions is given in Table 2.

As a control on the degree of refinement accomplished in solvent extraction operations, a brief examination in which only one or two extractions are taken is usually sufficient. Information so obtained will show whether or not an oil is free from material of lower API gravity than some specification point, as, for example, 20 API for an SAE-30 grade. Such freedom from material below a certain grade is found desirable to give oils of consistently high quality.

Many samples of commercial oils have been examined by the procedure described, and some typical composition curves are presented in Figure 2. The inspection data on these oils are given in Table 3. It will be noted that the curve for the Pennsylvania oil differs from the others, in that it shows a reversion in gravity towards the end. This is due to the very wide boiling range of this oil which is of the residual type. In the analytical solvent fractionation, the separation is, of course, accomplished by means of differences in solubility of the various materials comprising the oil. Since solubility of petroleum fractions is influenced to some extent by molecular weight, as well as by chemical composition, there is a tendency for the accumulation, in the final raffinate or in the later extract fractions, of materials of high molecular weight and viscosity. These fractions in the case of a Pennsylvania residual oil may be of such high molecular weight that they have a lower API gravity, even though they may have greater paraffinicity than the fractions immediately preceding them.

The curves in Figure 2 further serve to show the relatively narrow spread of composition of highly refined solvent extracted oils in comparison with either the Eastern oils refined by conventional methods or the Western or naphthenic type oils. This narrow range in composition is reached by the elimination in the solvent extraction process of all materials of less than a certain degree of paraffinicity and by the elimination in the dewaxing process of the most paraffinic hydrocarbons which would give a high pour point to the oil.

From the results presented, it is seen that laboratory multiple-batch extraction, when performed in accordance with the procedure described, gives valuable information on the composition of lubricating oils. When used for the analysis of lubricating stocks, the method permits a close estimation of the content of material of any prescribed quality. The

TABLE 2
Analytical Extraction Schedule for Finished Lubricating Oils

TEMPERATURES FOR ANILINE

Extraction No.	Volume Percent Solvent All SAE Grades	Extraction Temperature °F.						
		SAE-10	SAE-20	SAE-30	SAE-40	SAE-50	SAE-60	SAE-70
First	120	100	105	110	115	120	125	135
Subsequent extractions	100	All subsequent extractions at 10 deg. F. higher temperature than preceding extraction.						

Note: For blended oils containing residual stocks, begin fractionation at temperature in table for next lower SAE grade.

TEMPERATURES FOR CHLOREX

Extraction No.	Volume Percent Solvent All SAE Grades	Extraction Temperature °F.						
		SAE-10	SAE-20	SAE-30	SAE-40	SAE-50	SAE-60	SAE-70
First	120	40	45	50	55	60	65	70
Subsequent extractions	100	All subsequent extractions at 6 to 10 deg. F. higher temperature than preceding extraction.						

Note: For blended oils containing residual stocks, begin fractionation at temperature in table for next lower SAE grade.

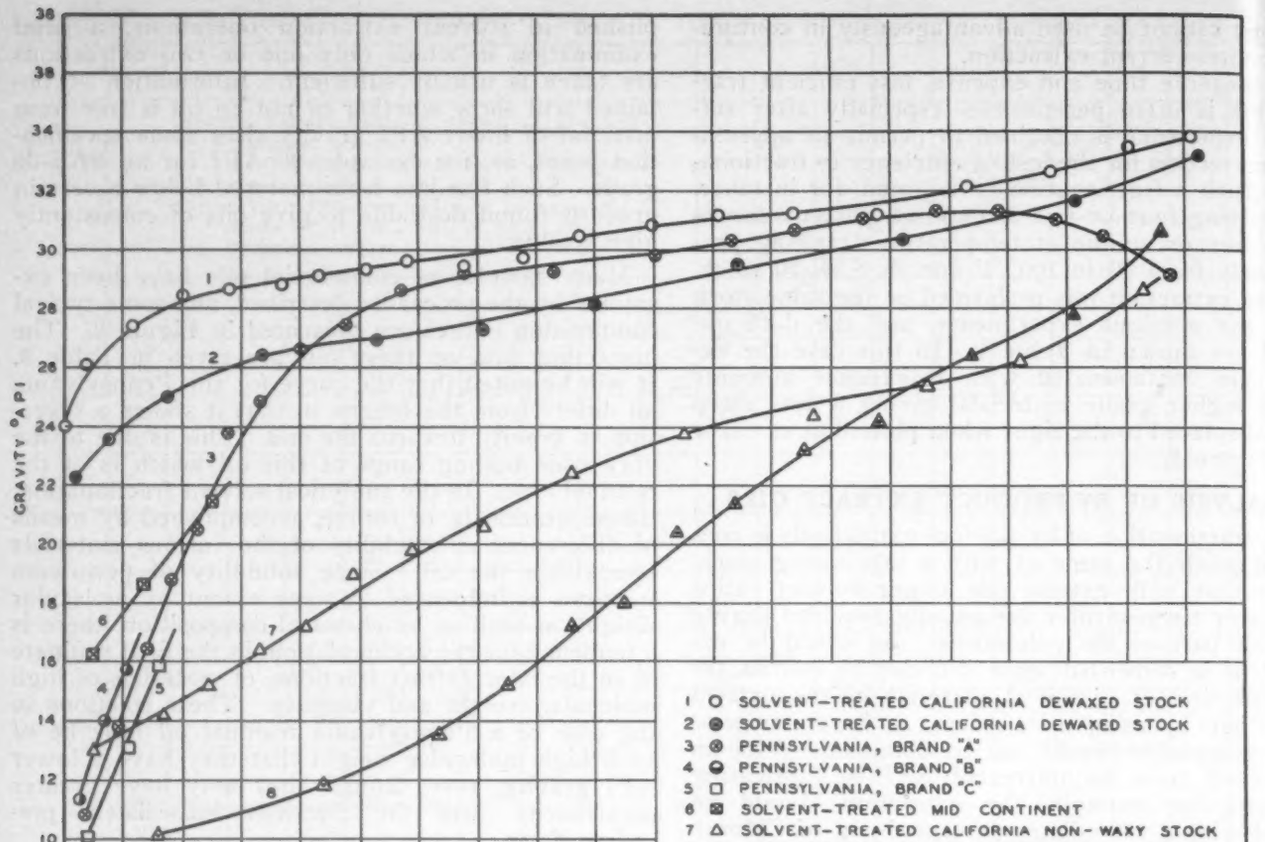
GRAVITY °API
PERCENTAGE BY VOLUME
1 SOLVENT-TREATED CALIFORNIA DEWAXED STOCK
2 SOLVENT-TREATED CALIFORNIA DEWAXED STOCK
3 PENNSYLVANIA, BRAND "A"
4 PENNSYLVANIA, BRAND "B"
5 PENNSYLVANIA, BRAND "C"
6 SOLVENT-TREATED MID CONTINENT
7 SOLVENT-TREATED CALIFORNIA NON-WAXY STOCK
8 ACID-TREATED CALIFORNIA NON-WAXY STOCK

FIGURE 2—*Solvent-Fractionation Curves of Finished Motor Oils.*

succesive extracts from a lubricating stock show a progressive change in chemical composition, as indicated by gravity, viscosity-gravity constant, viscosity index, etc., with the gravity usually ranging from less than 10 API to better than 30 API for stocks of intermediate viscosity. This wide variation in composition is so common that it appears practically all lubricating stocks contain the same components, and that the differences in the over-all properties of the respective stocks are due primarily to differences in the proportions of the components. It seems probable that the fractions having gravities below about 15 API are predominantly aromatic in character, while those ranging from about 15 to 20 API are essentially naphthenic. As the API gravity increases, however, the effect of any naphthenic portions of the hydrocarbon molecule probably becomes less prominent, and the paraffinic characteristics increase. The upper limit of API gravity for the so-called paraffinic lubricants corresponds to the point at which these compounds show a sufficiently high melting point to interfere seriously with the pour-point characteristics of the oil as a whole.

When applied to finished motor oils, the analysis shows the extent to which some components have been eliminated and others concentrated in the refining process. Considerable variation is found in this respect upon analysis of a wide variety of commercial motor oils.

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TABLE 3
Inspection Data on Finished Motor Oils Shown in Figure 2

Sample No.	Type	API Gravity at 60 °F.	Flash Point (Cleveland Open Cup) (°F.)	Fire Point (Cleveland Open Cup) (°F.)	Carbon Residue (Percent)	Color (NPA)	Viscosity, Saybolt Universal Seconds, at: 100 °F.	210 °F.	Viscosity Index	Viscosity-Gravity Constant
1	Solvent-treated California dewaxed stock	30.8	500	570	0.01	4	485	64.5	102	0.795
2	Solvent-treated California dewaxed stock	29.1	490	560	0.03	4½	630	70.0	94	0.805
3	Pennsylvania brand "A"	27.7	470	525	0.84	6½	672	74.0	100	0.813
4	Pennsylvania brand "B"	28.6	460	520	0.74	6½	627	73.0	104	0.807
5	Pennsylvania brand "C"	27.2	465	525	0.95	6	621	71.0	100	0.818
6	Solvent-treated Mid Continent	27.2	495	580	0.03	3	762	73.0	83	0.818
7	Solvent-treated California non-waxy stock	22.2	405	460	0.10	4½	970	68.5	29	0.858
8	Acid-treated California non-waxy stock	18.7	405	460	0.33	8	975	68.0	22	0.886

SERVICE CHARACTERISTICS OF Motor Oils *as Related to Composition*

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BY means of solvent fractionation, it has been possible to separate lubricating oil into typical classes of components characterized by different physical and chemical properties. The performance characteristics of these components have been studied with particular attention to:

1. Wear.

2. Sludge formation and other results of crankcase oxidation.

3. Carbon deposition as affecting the octane requirement of the engine.

The rate of wear has been found to be a function of the paraffinicity of the lubricating oil, with the low API gravity, high VGC components showing many times the wear of the highly paraffinic fractions. No difference was found between the wear characteristics of highly paraffinic oils of wide and narrow boiling range. Oxidation stability, reflected in service in reduced formation of sludge and acidity and less viscosity change, was found to be greatly improved by thorough removal of the components of low gravity and high viscosity-gravity constant.

The change in octane requirement, due to carbon deposition in service, has been compared for typical residual Pennsylvania oils and a highly solvent-treated oil of restricted boiling range. The average rate of carbon formation with the Pennsylvania oils was equivalent to an increase in octane requirement of one octane number for each 300 to 400 miles driven, until the increase was about 7 to 14 octane numbers—beyond which point little further change seemed to occur. With the solvent-treated oil of narrow boiling range, the increase was only about one point for each 1,000 miles—until an increase of two to four points occurred, after which further increase was very slow. From these results, it is concluded that, in order to produce oils giving low wear and sludge formation and also low carbon deposition, it is desirable to remove not only all components of low API gravity, but also the paraffinic components of highest boiling point.

This paper was presented at Fifth Mid-Year Meeting, American Petroleum Institute, Tulsa, May 16, 1935.

IN discussing the characteristics of lubricating oils refined by the use of selective solvents, the question is sometimes raised as to whether such solvents may not remove certain useful components, in consequence of which the solvent process oil may be deficient in lubricating value or, as commonly expressed, in oiliness. The purpose of the present paper is to present data on the service characteristics of some commercial lubricating oils and of lubricating oil fractions which may be taken as representing typical classes of components. From these data, the conclusion is drawn that the removal of the less paraffinic fractions by the use of selective solvents results in an improvement in the lubricating value of the oil, as well as in other characteristics. From such information on the characteristics of typical components, it is also possible to arrive at a general estimate of the service characteristics of a lubricating oil when its composition, as shown by solvent fractionation[1] methods is known.

Of the various functions of a lubricant, that of extending the useful life of the machine by reducing wear or preventing failure of parts in moving contact is unquestionably one of the most important. Although the higher operating temperatures in modern high-speed automobile engines have focused attention recently on problems of bearing lubrication and bearing composition, it is common experience that the repair costs on automobile engines are principally for overcoming the effects of wear, rather than the effects of mechanical failure.

Of the many tests which have been proposed for the examination of lubricating oils, by far the majority give results which are of value in characterizing the oil, but are only indirectly related to its lubricating value. The mechanical tests of lubricating oils for the most part fall into two classes; first, bearing tests such as the Navy work-factor test, in which the oil is subjected to moderately severe conditions of temperature and loading, and the changes occuring in the oil are subsequently determined by laboratory tests; and, second, bearing tests such as the Timken and Almen tests, in which the oil is subjected to increasingly severe load conditions until mechanical failure occurs, and the load at failure taken as an index of the quality of the oil. Tests of the first type, and laboratory tests in which the oil is subjected to the action of air or oxygen at a high temperature, give valuable indications of the changes which may occur in an oil in service, but give results

related only indirectly to the wear-preventing characteristics of a lubricant. Tests of the second type give indications as to the probability of mechanical failure from scoring or seizing occurring under extreme pressure conditions, but give little or no information on the wear to be expected at the lower bearing pressures which exist in automobile engines under normal service conditions.

The actual determination of wear in an automobile engine, either by micrometer measurement or by weighing the piston rings and pistons before and after a run, is laborious and time consuming, since runs of several thousand miles are required to obtain a readily measurable amount of wear. Furthermore, if the tests are made on different engines of the same make, there is always considerable uncertainty as to the extent of their similarity; or if successive long runs on a single engine are made, the average age of the engine, expressed in miles run, is so different for the different runs as to raise a question as to the validity of the comparison. These difficulties in determining engine wear are largely overcome by basing the determination upon the increase in iron content of the lubricating oil in the course of runs of moderate length, as suggested by Langdon.[3] The same general method has been employed at the Pennsylvania State College,[2] and in the Royal Dutch Shell laboratories [4] for investigating cylinder wear in Diesel engines. In the present work the increase in the iron content of the used oil has been employed exclusively as an index of the amount of engine wear; and the general uniformity of results in successive tests, together with a comparison of the results with measured wear under typical conditions, has been such as to justify considerable confidence in the validity of the method.

METHOD FOR DETERMINING WEAR THROUGH ANALYSIS OF THE USED OIL

In using the increase in iron content of the lubricating oil as an index of the wear occurring in an engine, it has been found necessary to follow a carefully defined procedure in order to obtain dependable results. If the engine is new, a breaking-in period equivalent to about 5000 miles of normal operation is required before consistent wear values can be obtained. In any case, the lubricating oil previously used, together with its content of iron, must be thoroughly flushed out before the test run is made. To accomplish this, the engine was first operated under standard conditions of temperature and load for a one-hour period on a portion of the test oil. This oil was drained out, and the engine operated for a three-hour period with a second portion of the test oil, after which the oil was again thoroughly drained out. The engine was then re-filled with the test oil and operated for a definite period, usually equivalent to 1000 or 1500 miles, under carefully controlled conditions of water and oil temperature, load, and speed. The first oil sample was taken at the end of 50 miles, a second sample at the middle of the test period, and the final sample at the end of the test peroid. In normal practice the original and final samples were used in the calculation of wear, and the intermediate sample was used only as a check. In taking these samples, extreme care was used to assure the samples being representative. All samples were taken from the circulating oil line while the engine was in operation. Triplicate samples of approximately 10 g. each were taken directly in tared-porcelain crucibles, and the samples burned without transferring. The iron content was then determined by the thiocyanate colorimetric method. To express the results on a uniform basis, a value referred to as the wear index, representing the amount of wear in milligrams of iron per 1000 miles of operation, was then calculated.

In developing the formula, it was assumed that, under the conditions of test:

1. Oil consumption is a straight-line function of miles of operation.
2. Iron wear is a straight-line function of miles of operation.
3. Oil consumed carries with it a proportional amount of iron.
4. Replacement oil, if added, is in small increments uniformly distributed over the run.

Based on these assumptions, the following approximate formula was derived:

$$W = \left[DI_2 - CI_1 + (C - D + R)\frac{(I_1 + I_2)}{2} \right] \frac{1000\,G \times 453{,}600}{4 \times 100\,(B - A)}$$

in which:

W=wear index, milligrams of iron per 1000 miles.
A=speedometer reading when first oil sample is taken, miles.
B=speedometer reading when final oil sample is taken, miles.
C=original volume of oil, quarts.
D=volume of oil drained, quarts.
R=volume of replacement oil, quarts.
G=density of original oil, pounds per gallon.
I_1=iron content of oil at *A*, percent by weight.
I_2=iron content of oil at *B*, percent by weight.

The formula just given may be reduced to the following form, which is that used in the calculations:

$$W = \left[(C + D)\,(I_2 - I_1) + R(I_1 + I_2) \right] \frac{567{,}000\,G}{B - A}$$

As a means of visualization, it is of interest that a wear-index value of 900 represents the removal through wear, in 1000 miles, of the amount of iron in a Gillette razor blade.

WEAR TESTS OF VARIOUS OILS UNDER CONDITIONS OF CONTINUOUS SERVICE

After preliminary tests had shown that this method of determining wear would give dependable results, a series of test runs was made on a motor dynamometer with a small six-cylinder engine of modern design, using typical Eastern and Western oils, and an experimentally produced solvent process oil produced from California waxy crude oil. In order to follow mechanical changes which might occur in the engine, runs were made at frequent intervals with a reference oil. The inspection data on all of the oils used in the work reported in this paper are given in Table 1, and data on the used oils from typical runs are given in Table 2. The wear indices obtained in this first series of dynamometer runs are given in Table 3. An examination of the individual wear-index values shown in Table 3 indicates that, although the reproducibility of the test is only moderate, the test definitely segregates different types of oil with regard to their wear-reducing ability. The Eastern oil and the solvent process oil have generally similar wear index values, while the typical acid-tested Western oil from asphalt base crude oil shows a definitely higher rate of wear.

FLEET TEST UNDER ROUTINE SERVICE CONDITIONS

The dynamometer tests just described were run under carefully controlled conditions of continuous operation. Since tests under laboratory conditions

TABLE 1
Inspection Data on Original Oils

Lubricant	Test Series	API Gravity at 60° F.	Viscosity Saybolt Universal Seconds, at: 100° F.	130° F.	210° F.	Viscosity Index	Viscosity-Gravity Constant*	Flash Point (Cleveland Open Cup) (° F.)	Fire Point (Cleveland Open Cup) (° F.)	Pour Point (° F.)	Conradson Carbon Residue (Percent)	Neutralization No. (ASTM)	Sulfur (Percent by Wt.)	Indiana Oxidation Test: Time for 10 Mg. Sludge (Hrs.)	Time for 100 Mg. Sludge (Hrs.)	Viscosity Increase (Percent)†
Oil E-1	First dynamometer	28.3	459	209	62.0	101	0.813	420	480	20	0.64	0.04	0.14	36	95	18
Oil W-1		20.7	700	261	59.2	15	0.874	370	435	0	0.18	0.13	0.57	7	33	64
Oil S-1		28.5	593	256	66.0	88	0.810	480	550	10	0.03	0.03	0.12	52	111	6
Oil E-2		28.5	493	224	64.4	102	0.810	445	500	20	0.52	...	...	54	107	20
Oil S-2		28.8	473	209	60.4	90	0.810	460	520	0	0.02	0.03	0.13	93	168	4
Oil T-1	Fleet test	29.1	530	234	63.4	90	0.807	485	535	15	0.05	0.02	0.16	103	239	4
Oil W-2		20.1	462	187	52.8	25	0.883	375	425	—10	0.13	0.07	1.33	8	24	77
Oil W-3		20.0	637	242	57.2	13	0.881	395	450	—10	0.16	0.08	0.73	11	36	49
Oil E-3	Second dynamometer	29.5	456	210	63.2	106	0.804	435	500	20	0.53	0.05	0.07	222	236	19
Oil T		28.9	506	222	62.2	90	0.809	455	530	5	0.05	0.03	0.15	91	187	3
AF-1		12.0	915	299	57.7	—70	0.949	350	400	15	0.63	0.20	1.22	...	...	...
AF-2		11.4	1,021	304	57.1	—117	0.955	335	395	10	0.73	0.08	1.16	3	18	122
Oil T+10 percent AF-2		27.1	512	223	61.0	82	0.822	430	505	10	0.07	0.04	0.25	11	44	25
Oil T+20 percent AF-2		25.3	527	224	60.0	71	0.837	390	465	10	0.16	0.05	0.35	5	23	29
Oil T+30 percent AF-2		23.1	547	228	60.0	65	0.854	400	465	—15	0.20	0.04	0.45	4	16	...
Oil T+50 percent AF-1		19.9	607	238	58.1	32	0.881	370	430	0	0.21	0.13	0.65	4	17	...
Oil T+70 percent AF-2		16.4	713	260	57.4	—10	0.910	365	410	0	0.32	0.09	0.86	3	11	...
Naphthenic fraction		19.7	698	262	59.8	22	0.882	405	475	—5	0.43	0.14	0.89	19	22	62
Oil T+50 percent naphtha		24.3	570	238	60.5	63	0.844	380	440	—5	0.18	0.08	0.51	15	33	59
Wax		34.7	...	...	70.0	...	0.765	...	...	165	0.40	0.07	0.14	...	...	...

* From viscosity at 210° F.
† Increase in kinematic viscosity at 130° F., after 50 hours of oxidation.

Distillation Tests at 1 Mm. Absolute Pressure

Lubricant	Observed Vapor Temperature at Indicated Percentage Recovered (° F.): Initial Boiling Point	5 Percent Point	10 Percent Point	15 Percent Point	20 Percent Point	25 Percent Point	30 Percent Point	35 Percent Point	40 Percent Point	45 Percent Point	50 Percent Point	55 Percent Point	60 Percent Point	65 Percent Point	70 Percent Point	75 Percent Point	80 Percent Point	85 Percent Point	90 Percent Point
Oil E-1	380	407	417	425	431	436	441	446	452	459	467	478	495	515	546	584	612	649	702
Oil E-2	410	424	432	438	444	449	454	460	466	474	482	496	511	534	562	593	645	690	745‡
Oil E-3	388	417	429	439	447	454	460	466	471	478	485	496	513	539	570	597	647	695	750‡
Oil T-1	418	450	456	462	466	471	477	482	488	494	500	508	516	526	536	546	556	569	584
Oil W-3	322	347	366	380	392	401	410	417	424	431	437	444	450	458	466	475	485	497	514
AF-1	288	332	362	385	403	418	433	444	455	462	469	472	474	476	476	474	473	479	480‡
Naphthenic fraction	314	352	379	397	411	421	429	435	440	444	448	454	459	464	471	478	487	497	510

‡ Extrapolated.

AF-1 — Aromatic fraction from California waxy crude oil, produced as an extract in sulfur dioxide treatment of a propane-dewaxed distillate, subsequently treated with 98 percent sulfuric acid and clarified by a light contact-clay treatment.

AF-2 — Aromatic fraction from California asphaltic crude oil, produced as an extract in sulfur dioxide-treatment of an acid-treated distillate and clarified by a light contact-clay treatment.

E-1, E-2 — Commercial Eastern or Pennsylvania oils containing residual fractions.

E-3 — Solvent-treated Pennsylvania oil, produced experimentally by treatment of oil "E-2" with sulfur dioxide.

Naphthenic fraction — Naphthenic fraction from California waxy crude oil, produced as a sulfur dioxide-benzene extract from a dewaxed and sulfur dioxide-treated distillate, and subsequently treated with 80 percent sulfuric acid and clarified by contact-clay treatment.

S-1, S-2 — Solvent process oils from California waxy crude oil, produced experimentally by treatment of propane-dewaxed distillate with sulfur dioxide followed by sulfur dioxide benzene, and with a final contact-clay treatment.

T, T-1 — Commercial solvent process oils from California waxy crude oil, produced similarly to "S-1" and "S-2".

W-1 — Commercial Western oil, produced by acid and sulfur dioxide-treatment of a distillate from California asphaltic crude oil.

W-2, W-3 — Commercial Western oils, produced by acid treatment of distillates from California asphaltic crude oil.

Wax — Commercial petrolatum of 164° F. melting point and about 11 percent oil content.

do not always agree with results obtained under actual service conditions, a test was made with 20 passenger automobiles and light trucks from the fleet of one of the large public utility corporations in southern California. These cars were run under routine service conditions of intermittent operation for successive test periods of 1000 miles, and samples for determination of wear index were taken in the same way as in the dynamometer runs. A run was first made in each car with either of two well known brands of oil produced by acid treatment of distillate from California low pour-point crude oil, and then one or more runs were made with a solvent extracted oil commercially produced from California waxy crude oil. This oil for convenience is referred to hereafter as oil "T." The wear data obtained are shown in Table 4. It will be seen that on the average the Western acid-treated oils gave about 70 percent more wear than did oil "T." Unfortunately, time did not permit extending this fleet test to include the use of typical solvent-treated Eastern oils; but, from the similarity of the relationships of the wear indices in these fleet tests to the relationship found in the dynamometer tests, it is probable that such Eastern oil would have shown a wear index value very similar to that obtained with oil "T."

A comparison of the wear index values obtained in the fleet test and in the motor-dynamometer tests indicates a value over 10 times greater under the fleet test operation. This is undoubtedly due to the fact that, in the dynamometer tests, the runs were continuous; whereas, in the fleet test, the driving was intermittent and the engines cooled down at intervals in the course of each run. As pointed out by Williams,[5] the greatly increased wear at low engine temperatures, as in starting, appears to be due largely to the condensation, on the cold cylinder walls, of moisture which carries acidity.

The larger amounts of wear found in the fleet test are more comparable with general service experience, as would be expected. For comparison, it may be assumed that the wear occurring in the cylinders in short run passenger car service in 40,000 miles is equivalent, in a typical case, to a uniform wear of 0.005 inch of diameter, and that half of the weight of iron removed is from the piston rings and half

TABLE 2
Inspection Data on Typical Used Oils

LUBRICANT	Test Series	Miles Run	API Gravity at 60° F.	Viscosity, Saybolt Universal Seconds, at 130° F.	Pour Point (° F.)	Indiana Precipitation No. (Milligrams per 10 G.)	ASTM Precipitation No. (Milligrams per 10 G.)	Ash (Percent by Weight)	Conradson Carbon Residue (Percent)
Oil E-1	First dynamometer	1,000	28.4	182	15	24.1	0.08	0.090	0.83
Oil W-1		1,000	20.8	317	—10	25.8	0.23	0.020	0.50
Oil S-1		1,000	28.0	252	15	16.7	0.06	0.017	0.10
Oil E-2		1,000	...	...	...	12.1	0.03	...	0.84
Oil S-2		1,000	29.2	179	5	19.7	0.02	0.020	0.25
Oil T-1	Fleet test	1,100	28.6	142	5	30.7	0.20	0.06	0.37
Oil W-2		1,100	20.5	123	—20	63.5	0.35	0.08	0.80
Oil W-3		1,100	20.3	159	—20	69.4	0.37	0.07	0.89
Oil E-3	Second dynamometer	1,500	28.7	213	20	12.6	0.05	0.005	0.99
Oil T		1,500	28.9	194	5	10.4	0.07	0.005	0.21
AF-2		1,160	8.9	945	25	254	2.40	0.083	4.35
Oil T+10 percent AF-2		1,500	26.9	225	10	39.8	0.33	0.009	0.53
Oil T+20 percent AF-2		1,500	25.3	240	10	53.5	0.40	0.013	0.61
Oil T+30 percent AF-2		1,500	23.1	289	—10	90	0.70	0.020	1.12
Oil T+50 percent AF-1		1,500	20.3	304	0	68.7	0.52	0.073	1.06
Oil T+70 percent AF-2		1,500	15.5	506	0	221	2.20	0.040	2.64
Naphthenic fraction		1,500	18.7	321	—5	47.3	0.40	0.020	1.62
Oil T+50 percent naphtha		1,500	24.0	237	—10	19.9	0.15	0.019	0.61
Wax		1,500	33.7	67*	...	...	0.90	0.030	0.81

* At 210° F.

from the cylinder walls. By calculation, it is found that in a small sized engine this amount of wear is equivalent to a wear index value of about 1400 mg. of iron per thousand miles of travel. This figure lies well within the range of values for oil "T" in the fleet test, as given in Table 4. This satisfactory agreement is taken as corroborating the opinion that the method of determining wear by analysis of a lubricating oil gives significant and valuable results.

Since the amount of wear in the fleet test is comparable with service experience, a question might be raised as to the significance of the much smaller wear indices found in the dynamometer test. It will be noted, however, that in both cases the average wear with the Western or naphthenic-type oils was about 60 percent more than with the paraffinic solvent process oils produced from California waxy crude oil. The constancy of this ratio of wear is believed to indicate that the relative amount of wear under any particular set of operating conditions is significant, but that the absolute values of the wear index may be expected to vary markedly with the size and type of engine and the conditions of service.

WEAR TESTS ON PREPARED COMPONENTS OF LUBRICATING OILS

Since both the motor-dynamometer and the fleet tests indicated a decided difference between the various oils in their ability to reduce wear, the next step in the investigation was an attempt to identify more definitely the constituents that either caused wear or had a low efficiency in preventing wear. For this purpose, a series of oils of varying paraffinicity was prepared. The oils were not produced from the same lubricating distillate, but rather were produced from similar lubricating distillates of appropriate viscosities, so that all of the oils had about the same viscosity at the crankcase temperature, viz., about 100 sec., Saybolt Universal, at 170°F.

In the case of the least paraffinic fraction, two samples were prepared. One sample, designated as aromatic fraction "AF-1," was an extract produced by sulfur-dioxide treatment of a propane-dewaxed distillate from California waxy crude oil. Because of its very dark color, it was given a moderate treatment with 98 percent sulfuric acid, neutralized, and clarified by a light contact-clay treatment. The other

TABLE 3
Wear Characteristics of Various Oils as Shown by First Series of Dynamometer Runs
(Runs made on a small six-cylinder engine operating on a variable load and speed cycle equivalent to approximately 40 miles per hour road travel.)

LUBRICANT	Run No.	Characteristics of Original Oil			Indiana Precipitation No. of Used Oil (Milligrams per 10 G.)	Wear Index (Milligrams of Iron per 1,000 Mi.)	Average Wear Index	Relative Wear Index* (Percent)
		Viscosity Index	Viscosity-Gravity Constant	Indiana Oxidation Test (Time for 10 Mg. Sludge) (Hours)				
Oil E-1	8	101	0.813	36	16.7	168	...	...
	11	...	...	..	15.2	218	...	...
	13	...	...	..	29.2	195	...	...
	16	...	...	..	33.1	145	184	100
	18	...	...	..	25.9	177	...	...
	21	...	...	..	24.1	200	...	...
Oil W-1	12	15	0.874	7	25.8	263	...	...
	15	...	...	..	41.6	245	252	137
	19	...	...	..	58.4	182	...	...
	23	...	...	..	45.4	318	...	...
Oil S-1	10	88	0.810	52	16.7	132	...	...
	14	...	...	..	19.8	154	145	79
	20	...	...	..	23.7	150	...	...
Oil E-2	38	102	0.810	54	...	100†	...	...
	39	...	...	..	19.1	68†	84†	100†
Oil S-2	36	90	0.810	93	19.7	64†	...	...
	37	...	...	..	...	95†	79†	94†

* $\frac{\text{Wear index of test oil}}{\text{Wear index of reference oil}} \times 100$. Oil "E-1" was used as reference oil in this series, except for the last four runs.
†Under slightly different operating conditions from previous tests.

TABLE 4

Results of the Fleet Test to Compare Wear with Oils "W-2" and "W-3" Against Oil "T-1"

Car Make and Number	Wear Index, Milligrams of Iron Per 1,000 Miles							Relative Wear Index* (Per Cent)	Relative Wear Index for Each Make (Percent)	Relative Wear Index for All Cars (Per Cent)
			Oil T-1							
	Oil W-2	Oil W-3	First 1,000 Miles	Second 1,000 Miles	Average, Oil W-2	Average, Oil W-3	Average, Oil T-1			
Make A No. 1	1,492	....	1,035	....	...	...	...	144	....	....
No. 2	2,770	...	1,252	1,189	...	...	...	227	....	....
No. 3	1,196	...	854	908	...	...	...	136	....	...
No. 4	1,167	...	941	...	2,164	6,475	1,503	124	....	...
No. 5†	....	6,475	3,525	...	...	...	...	184	164	...
No. 6	1,858	...	1,656	...	...	...	...	112	....	...
No. 7	2,013	...	962	...	...	...	...	209	....	...
No. 8	4,700	...	3,070	...	...	...	...	153	....	...
No. 9	2,120	...	1,144	...	...	...	...	185	....	...
Make B No. 1†	....	2,139	2,329	1,687	...	...	...	106	....	...
No. 2	....	3,015	1,915	...	...	2,451	2,299	157	110	171
No. 3	....	2,200	3,265	...	...	...	...	67‡	....	...
Make C No. 1	3,255	...	2,135	2,050	...	...	...	155	....	...
No. 2	2,685	...	1,030	1,270	...	...	...	233	....	...
No. 3	2,270	...	1,775	1,725	3,681	...	1,737	130	201	...
No. 4	7,680	...	2,460	...	...	...	...	312	....	...
No. 5	2,513	...	1,453	...	...	...	...	173	....	...
Make D No. 1	....	1,189	567	636	1,379	...	734	198	189	...
No. 2	....	1,570	932	803	...	...	...	181	....	...
Make E No. 1	....	1,653	718	659	...	1,653	688	240	240	...

* Wear index of test oil / Wear index of reference oil × 100. Oil "T-1" was used as the reference oil.
†One and one-half ton truck.
‡Although at variance with the other results, this figure has been included in the averages.
Make "A" is a small six-cylinder car.
Make "B" is a small eight-cylinder car.
Make "C" is a small four-cylinder car.
Make "D" is a small six-cylinder car.
Make "E" is a small six-cylinder car.

sample, "AF-2," was produced by application of liquid sulfur dioxide to a commercial acid-treated Western oil from California asphaltic crude oil. The extract obtained was given a light contact-clay treatment in order to remove any suspended impurities.

The oil next in order of paraffinicity, and referred to as the naphthenic fraction, was prepared as an intermediate extract from a propane-dewaxed distillate from California waxy crude oil. This intermediate extract was produced by extracting, with sulfur dioxide and benzene, a dewaxed distillate which already had been treated with liquid sulfur dioxide to remove the compounds of very low paraffinicity. The intermediate extract was given a light treatment with 80 percent sulfuric acid, neutralized, and contact-clay treated.

The fraction representing a paraffinic lubricating oil was the commercially produced solvent-extracted oil of appropriate viscosity from California waxy crude oil, referred to previously as oil "T." For comparison, a solvent-extracted Eastern oil was prepared by treatment of a commercial Pennsylvania oil with sulfur dioxide under conditions causing the removal of about six percent of 11.3-A.P.I. extract of a very

TABLE 5

Wear Characteristics of Various Oil Components in Second Series of Dynamometer Runs

(Runs made on a small six-cylinder engine operating under constant load and speed equivalent to 40 miles per hour road travel, but with the throttle closed momentarily every 20 minutes.)

LUBRICANT	Run No.	Characteristics of Original Oils			Indiana Precipitation No. of Used Oil (Milligrams Per 10 G.)	Wear Index (Milligrams of Iron Per 1,000 Miles)	Average Wear Index	Relative Wear Index* (Per Cent)
		Viscosity Index	Viscosity-Gravity Constant	Indiana Oxidation Test (Time for 10 Mg. Sludge) (Hours)				
Oil E-3	1	106	0.804	222	13	141		
	3	...	....	...	11	86		
	8	...	....	...	8	75		
	13	...	....	...	12	83		
	16	...	....	...	20	141		
	19	...	....	...	18	94	101	100
	20	...	....	...	5	61		
	22	...	....	...	7	111		
	24	...	....	...	4	89		
	27	...	....	...	6	147		
	28	...	....	...	3	70		
Oil T	2	90	0.809	91	10	112		
	7	...	....	...	17	80	94	93
	10	...	....	...	15	89		
AF-2	4	—117	0.955	3	...	800		
AF-2	18	...	....	...	254	608	704	697
Oil T+10 percent AF-2	21	82	0.822	11	40	110	110	109
Oil T+20 percent AF-2	23	71	0.837	5	53	120		
Oil T+20 percent AF-2	25	...	....	...	56	116	118	117
Oil T+30 percent AF-2	17	65	0.854	4	90	166		
Oil T+30 percent AF-2	26	...	....	...	82	123	145	144
Oil T+50 percent AF-1	30	32	0.881	4	69	222	222	220
Oil T+70 percent AF-2	15	—10	0.910	3	221	360	360	356
Naphthenic fraction	9	22	0.882	19	47	216		
Naphthenic fraction	12	...	....	...	70	238	227	225
Oil T+50 percent naphtha	29	63	0.844	15	20	135	135	134
Wax	11	...	0.765	...	...	73		
	14	...	....	...	...	106	89	88

* Wear index of test oil / Wear index of reference oil × 100. Oil "E-3" was used as reference oil in this series.

low degree of paraffinicity, as shown by its viscosity-gravity constant of 0.944.

As an example of a hydrocarbon mixture of the highest degree of paraffinicity, a commercial petrolatum of low oil content was employed. The choice of a wax of this character was necessary in order to obtain material of comparable viscosity at the crankcase temperature.

The results obtained when using these various oil constituents in the dynamometer test engine are shown in Table 5. A different engine and slightly different operating conditions were used in this series of runs; and the results are, therefore, not directly comparable with those of the first dynamometer series. In the case of the aromatic fraction, the first run gave such an exceedingly high wear index, and the general condition of the motor was so bad that it was considered desirable to examine the effect of this material in detail. The solvent-process oil (oil "T") from California waxy petroleum was found by analytical solvent fractionation to contain no detectable amount of the aromatic fractions and was, therefore, used as a base stock to which various percentages of the aromatic fractions were added. In the tests on these blends, the wear index increased in proportion to the percentage of aromatic fractions present. The general form of this relationship is shown in Figure 1. At lower concentrations, the increase in wear index value with increase in aromatic-fraction content is relatively moderate as compared with the very rapid increase in wear-index value over the higher range. The blends produced from the aromatic fractions from the two types of California crude oil had similar effects on engine wear. The

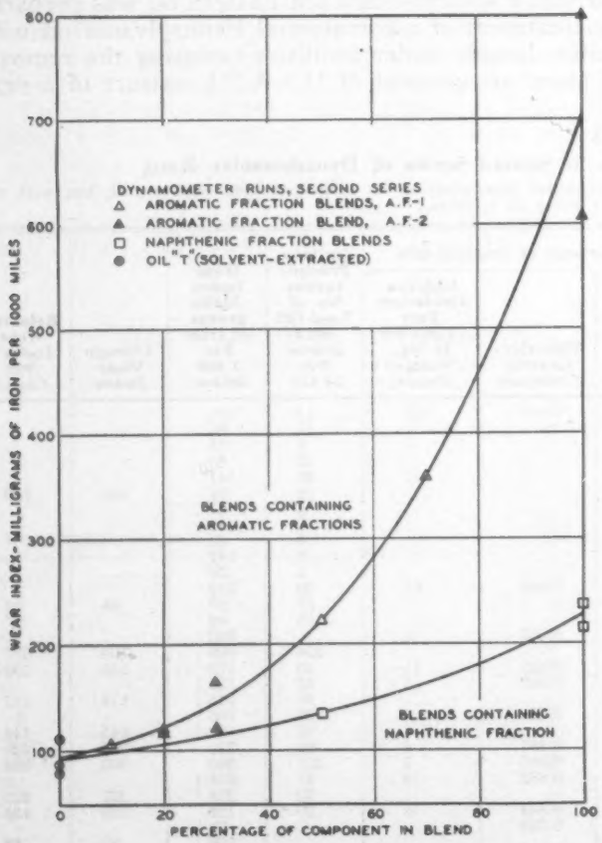

FIGURE 1

The Effect on Engine Wear of Aromatic and Naphthenic Fractions in Blends with Oil "T".

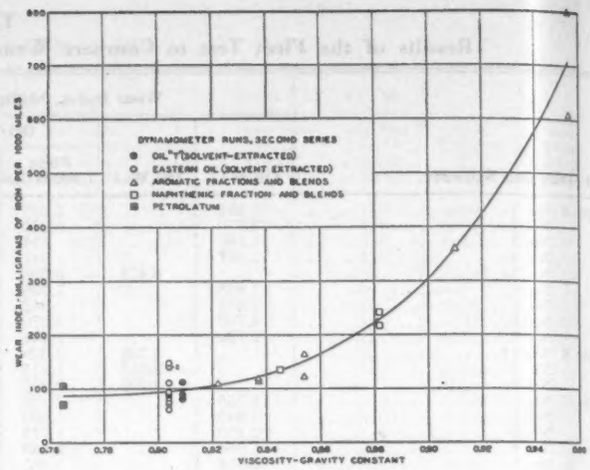

FIGURE 2

Engine Wear as a Function of the Viscosity-Gravity Constant of the Lubricating Oil.

similarity of the aromatic fractions from the two sources is also evident from the inspection tests.

In studying the effect of the naphthenic fraction, oil "T" was again used as the base stock in preparing an intermediate blend. As shown in Figure 1, the naphthenic fraction is not so effective as a lubricant as the paraffinic fractions—although it is greatly superior to the aromatic fractions.

In the tests with the wax it was necessary, of course, to melt the material before adding it to the engine, and to keep the crankcase at the full operating temperature during the course of the run. Aside from the fact that the physical characteristics of wax are such that it cannot be used conveniently as a lubricant under normal conditions, the test results indicate that it has good lubricating properties.

RELATIONS BETWEEN OBSERVED WEAR AND COMPOSITION

Although sufficient work has not yet been done to establish the relationship conclusively, the present results indicate that the lubricating value, as shown by the wear index, is closely related to the paraffinicity of the oil as expressed conveniently by the viscosity-gravity constant. As the viscosity-gravity constant decreases, the wear index decreases and appears to approach a constant value. The approximate constancy appears at a viscosity-gravity constant of about 0.810 and, as shown in Figure 2, very little further reduction in wear occurs with the use of oils having viscosity-gravity constants below this value.

In connection with this observed relationship between rate of wear and paraffinicity, the recent work of Dover and Hensley[6] is of interest. They have shown that the coefficient of dynamic friction of a certain aromatic compound, di-meta-tolyl ethane, is over twice that of a paraffinic hydrocarbon of generally similar physical properties, normal octadecane. The viscosity-gravity constants of these two compounds have been calculated to be 0.972 and 0.773, respectively, using the revised formula for low-viscosity oils, developed in this laboratory.[7] Although this work of Dover and Hensley pointed towards lubricating value, expressed in their case as coefficient of dynamic friction, as being a function of paraffinicity, it seemed desirable to investigate the possibility that the variation in observed wear might be

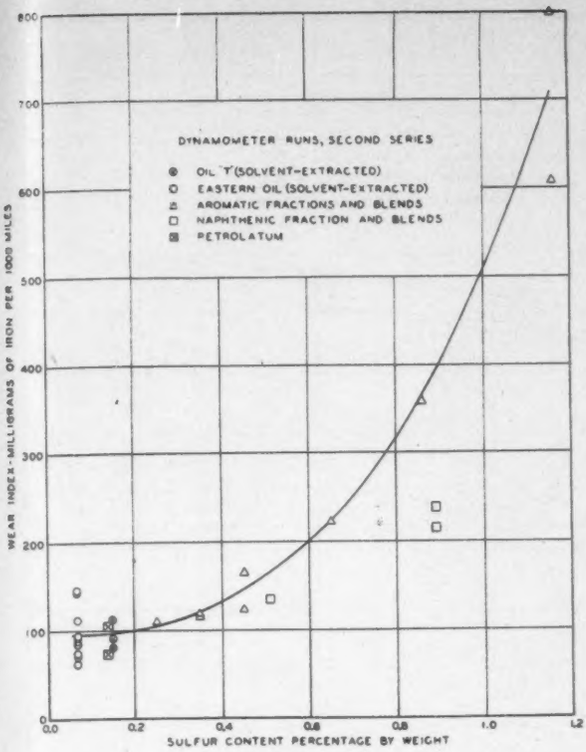

FIGURE 3
Engine Wear in Relation to the Sulfur Content of the Lubricating Oil.

due, in part at least, to some other factor, such as development of acidity or to differences in sulfur content.

An attempt to develop a relationship between the wear indices and the acid content of the used oils was unsuccessful when the comparison was made with neutralization numbers determined by the ASTM methods for either uncompounded or compounded oils. The difficulty in applying these methods to the analysis of dark colored oils may have tended to obscure a relationship, but it seems doubtful in any case whether corrosion from such acidity could have been a major factor in the observed wear, in view of the limited amounts of acids formed and the low activity of such acids. Because of the uncertainty of the results, as well as their apparent lack of significance, the values have not been included in the tables.

The possibility of a relationship between the wear index and sulfur content was suggested by experience with the use of sulfur in various forms in extreme-pressure lubricants. It is well known that one difficulty in using many effective extreme-pressure bases, including some sulfurized compounds, has been excessive wear. The theory is commonly held that the effectiveness of an extreme-pressure lubricant is due to formation under such conditions of service of a film of corrosion products which prevents seizure from metal-to-metal contact. In view of this, the question may be raised as to whether such high wear is not a normal accompaniment of great effectiveness in raising the film strength under extreme-pressure conditions.

When tested in an extreme-pressure testing device, the aromatic fractions were, in fact, found to have a relatively high film strength, as would be expected from their sulfur content. On plotting the wear indices of the various blends of aromatic and naphthenic fractions against the sulfur content of these blends, results as shown in Figure 3 were obtained. Although the values for the blends containing aromatic fractions appear to indicate a relationship between wear and sulfur content, the validity of this relationship is brought into question by the marked deviation of the naphthenic blends from the curve. It is possible that this deviation is due to differences in the activity of sulfur in different forms of combination, but it appears much more probable that it is the low paraffinicity of the aromatic fractions, rather than the sulfur content, which is responsible for the poor lubricating value of these fractions.

APPROXIMATE COMPOSITION OF VARIOUS LUBRICATING OILS

In Figure 4 the results are shown of solvent fractionation of the several prepared components, as well as for most of the commercial oils used in the investigation. The viscosity-gravity constant is taken as the most useful index of composition for the present purpose, because it is much more nearly an additive function than is viscosity index, for example. It has the further advantage of being a valid index of paraffinicity over a very wide range of molecular weight, viscosity, or boiling point. From a study of Figure 4, it is at once evident that the naphthenic fraction, which is very similar in composition to the typical sulfur-dioxide-treated Western oil "W-1," shows considerable overlapping of the aromatic and paraffinic fractions in its composition. Without more complete knowledge of the chemical composition of the hydrocarbons composing lubricating oils, it is not possible to establish a chemically-correct classification. The division into aromatic, naphthenic, and paraffinic fractions is, however, a very useful one; and it is also convenient to establish arbitrary points of division in terms of viscosity-gravity constant between these three groups of hydrocarbons. Based on the examination of various samples of extract produced by the use of sulfur dioxide under conditions of good fractionation, a viscosity-gravity constant of about 0.91 is chosen as the approximate dividing point between the aromatic fractions and the naphthenes. Also, from examination of solvent-extracted oils produced under conditions of good fractionation from California dewaxed lubricating distillates, it appears that the division point between paraffinic fractions—representing the major component of a paraffin base lubricating oil—and naphthenic fractions—representing the major components of a naphthene base or asphaltic base lubricating oil—should lie somewhere between 0.83 and 0.87 viscosity-gravity constant. For the present purpose, 0.86 viscosity-gravity constant has been arbitrarily chosen as the dividing point.

It may be seen from the fractionation curves that the aromatic-fraction sample contained only about 10 percent of naphthenic constituents, as defined by these arbitrary cutting points; and the paraffinic oil contained no aromatic or naphthenic constituents. The naphthenic fraction, however, contained about 25 percent of material of higher viscosity-gravity constant than 0.91 and about 30 percent of material of lower viscosity-gravity constant than 0.86. That the 25 percent of material of high viscosity-gravity constant was not alone responsible for the high wear

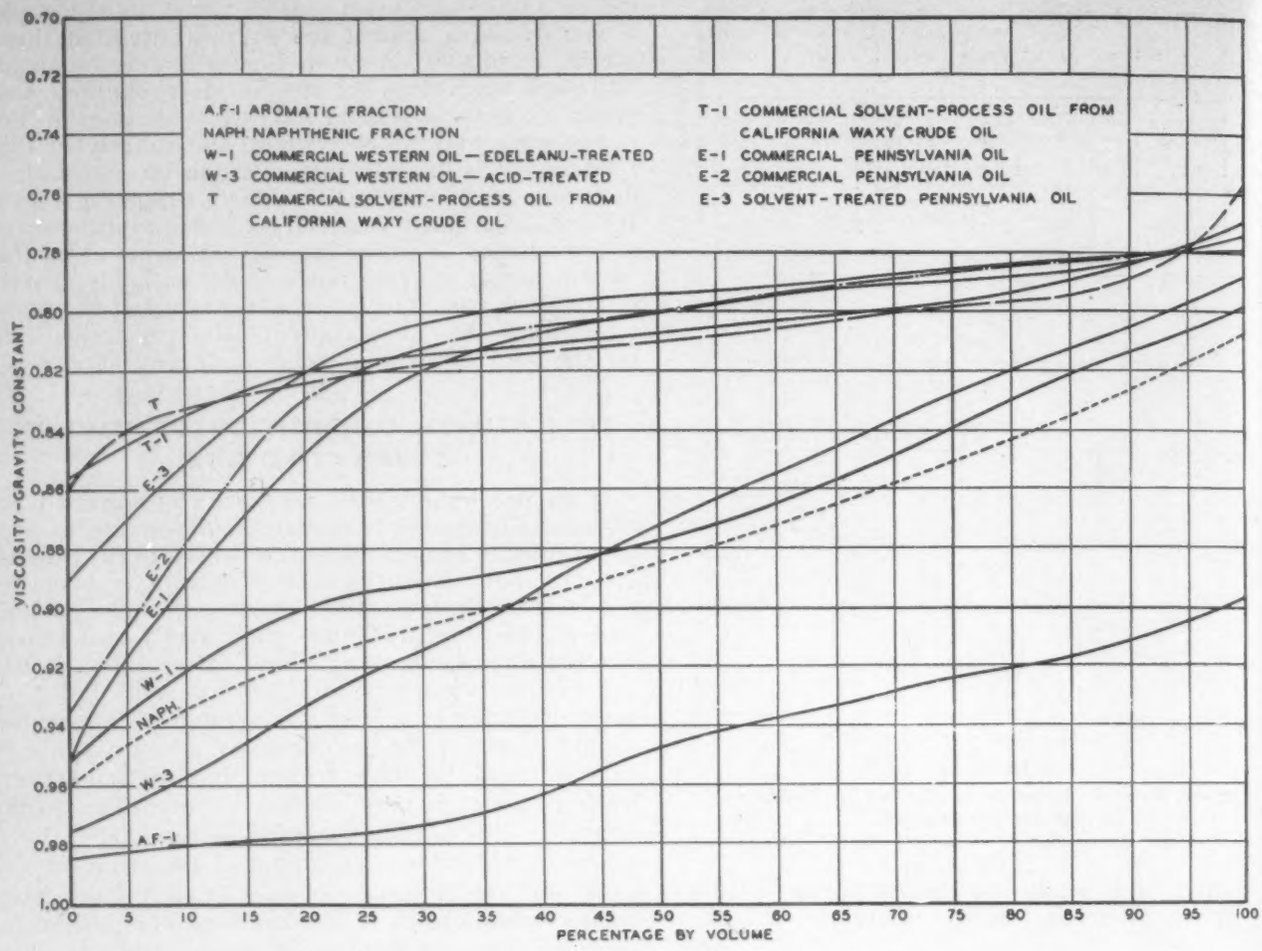

FIGURE 4
Solvent-Fractionation Curves of Various Oils.

index shown by the naphthenic fraction is indicated by the fact that this wear index is about the same as the wear index of a 50 percent blend of the aromatic fraction with oil "T." Since the effect of the aromatic constituents is undoubtedly offset to some extent by the paraffinic constituents also present, it is believed that the wear index actually found for the naphthenic fraction can be taken as an approximation to that for a naphthenic fraction lying substantially within the arbitrary limits of viscosity-gravity constant.

On examining the fractionation curves for the commercial oils, it may be readily seen that this method of analysis gives valuable information on the composition of the oils. Thus oil "T" is shown to lie entirely in the range of viscosity-gravity constants less than 0.86 and to contain no aromatic or naphthenic fractions as arbitrarily defined; and the solvent-treated Pennsylvania oil is shown to contain no aromatic fractions and only eight percent of naphthenic fractions. Since the wear index of the naphthenic component was found to be roughly twice that of the paraffinic oil "T," the effect of the naphthenic material in the limited proportion present in this solvent-extracted Eastern oil would be expected to be relatively small. The two commercial Eastern oils produced by conventional methods without the use of solvent extraction are shown to contain about five percent of material lying in the aromatic range, and also about 10 percent of material in the naphthenic range. In view of the results of tests on the blends of aromatic and naphthenic fractions with oil "T," the conclusion seems well justified that the removal, by solvent extraction, of the aromatic components, together with a part or all of the naphthenic components, results in improvement, rather than reduction, in lubricating value. The solvent-fractionation curves of the sulfur dioxide-treated Western oil "W-1" and the acid-treated Western oil "W-3" are of interest. It is seen that, particularly in the case of the acid-treated oil, relatively large amounts of aromatic material are present; and it would, therefore, be expected that such oils would show high rates of wear in comparison with highly purified paraffinic oils. This is in accordance with actual findings in both the dynamometer and fleet tests.

OXIDATION RESISTANCE OF LUBRICATING OILS IN RELATION TO COMPOSITION

For satisfactory performance, it is obviously necessary that a motor oil not only have desirable characteristics when new, but also that it retain these characteristics in service. One of the most important factors causing deterioration in service is oxidation; and resistance towards oxidation is, therefore, a very desirable characteristic. The effectiveness of solvent treatment in increasing the resistance of lubricating oils towards oxidation is well recognized, and in the

present work an attempt was made to relate oxidation stability more definitely to composition. Deterioration of a lubricating oil by oxidation may be readily followed by the increase in sludge content, carbon residue, viscosity, and acidity. In the Indiana oxidation test, chief reliance is placed upon a gravimetric-precipitation test for determination of sludge content, and upon viscosity increase—although the neutralization value may also be followed.

Indiana oxidation tests have been run on the various oils used in this investigation, and the results of these tests are given in Table 1. From these results, some interesting conclusions can be drawn. As might be expected, the aromatic fraction "AF-2" has especially poor oxidation stability, as shown both by the short time of three hours required for formation of 10 mg. of sludge per 10-g. sample and the large increase of 122 percent in the kinematic viscosity at 130° F. after 50 hours of oxidation. It is of particular interest that the addition of only 10 percent of this material to oil "T" reduced the stability from high value, represented by 91 hours and three percent viscosity increase, to 11 hours and 25 percent viscosity increase. This may be compared with the results shown for wear index, in which case the addition of 10 percent of aromatic fractions caused only a moderate increase in the amount of wear. From these results, it may be concluded that the complete removal of material of high viscosity-gravity constant by thorough solvent treatment is particularly desirable from the standpoint of improvement in oxidation stability. This is also shown by a comparison of the Indiana test results on the solvent-treated Eastern oil "E-3" with a corresponding Eastern oil "E-2" which had not been solvent-treated. It is seen that the removal of about six percent of low grade material raised the time required for formation of 10 mg. of sludge from 54 to 222 hours, but had no appreciable effect on the viscosity increase—which was about 20 percent in 50 hours.

A comparison between the solvent-extracted Eastern oil "E-3" and the solvent-extracted oil from California waxy crude oil, "T-1," is of interest in showing the differences in oxidation characteristics between oils containing residual stocks and oils composed exclusively of distillates. It is seen that oil "E-3" had a very long life before the formation of 10 mg. of sludge; but that when sludging once started, it proceeded very rapidly, as shown by the short time for the amount of sludge to increase from 10 to 100 mg. With oil "T-1," the time required for formation of 10 mg. of sludge was shorter; but the rate of sludge formation after reaching the 10-mg. point was still very slow, so that over twice as much time was required for formation of 100 mg. as for 10 mg. In consequence the total time required for formation of 100 mg. of sludge was approximately the same for the two oils. A relatively slow on-set of sludge formation in the Indiana test but a rapid formation after it once starts is a common characteristic of highly-treated lubricating oils containing residual stocks, and it is a further characteristic of such oils that the early evidences of deterioration during the progress of the oxidation often take the form of viscosity increases, rather than sludge formation. This is shown in the present instance by the viscosity increase of 19 percent in 50 hours for oil "E-3," in comparison with an increase of only four percent for oil "T-1" in the same length of time. The statement is made by the originators[8] of the Indiana test that laboratory sludging times well above 70 hours have little significance for comparative purposes, and viscosity change then becomes the primary consideration. It is difficult to evaluate quantitatively the sludging which takes place in a crankcase during service, but inspection of crankcases of engines used in the various road and dynamometer tests has shown that the high stability of the solvent-treated oil "T," indicated in the Indiana test, is actually reflected in service; and that the crankcases, valve chambers, and other places where gummy deposits usually accumulate are, in fact, exceptionally clean when this oil is used.

The data on the neutralization values of the used oils from the various test runs, although not very conclusive, gave some indication of a trend towards lower acid numbers for the oils of lower viscosity-gravity constants; from which it may be concluded that solvent refining, at least if not carried beyond the present limits of about 0.80 viscosity-gravity constant, is advantageous from the standpoint of reducing formation of acidity in service.

CARBONIZATION CHARACTERISTICS OF LUBRICATING OILS IN AUTOMOBILE ENGINES

In addition to satisfactory wear preventing and non-sludging characteristics, a lubricating oil for use in internal combustion engines should preferably exhibit minimum carbon deposition. It is well known that in gasoline engines the major proportion of the carbon on the cylinder heads and pistons is derived from the lubricating oil, and that the presence of this carbon induces knocking, and often necessitates the use of fuel of higher octane rating than if the engine were clean. In fact, the increase in octane requirements of an engine on continued service appears to be one of the most tangible elements of motor performance which the average motorist can evaluate. For this reason, it seemed desirable, in undertaking an investigation of the carbon-depositing characteristics of certain motor oils, to base the comparison upon the change in octane requirements of the engine, rather than to measure carbon deposition by collecting and weighing the deposits. This method of following carbon deposition was employed by Hawley and Bartholomew[9] who observed an increase in octane requirements from 64 to 80 octane number during 200 hours' operation of a test engine, with very little increase thereafter. Simultaneously the power output decreased about four percent. It is understood that the oil used in this test was a high quality paraffin base oil of SAE-30 grade.

In the present work on carbonization characteristics, 12 automobiles were operated under conditions of routine service. Each car was run on two types of oil; one the highly solvent-treated oil from California waxy crude oil, and the other comprising representative brands of high grade Pennsylvania oils containing residual stocks. Oil changes in all the cars were made at the same mileage intervals. In eight of the cars chosen for the test, the valves were ground and the combustion chambers cleaned thoroughly of all previous carbon deposits before beginning the test on each of the two types of oil. With the other cars, care was taken to insure that the engines had been run for a period of at least 8000 miles on high grade Pennsylvania oil since the carbon had been removed. Then, without disturbing the conditions in the combustion chamber, the Penn-

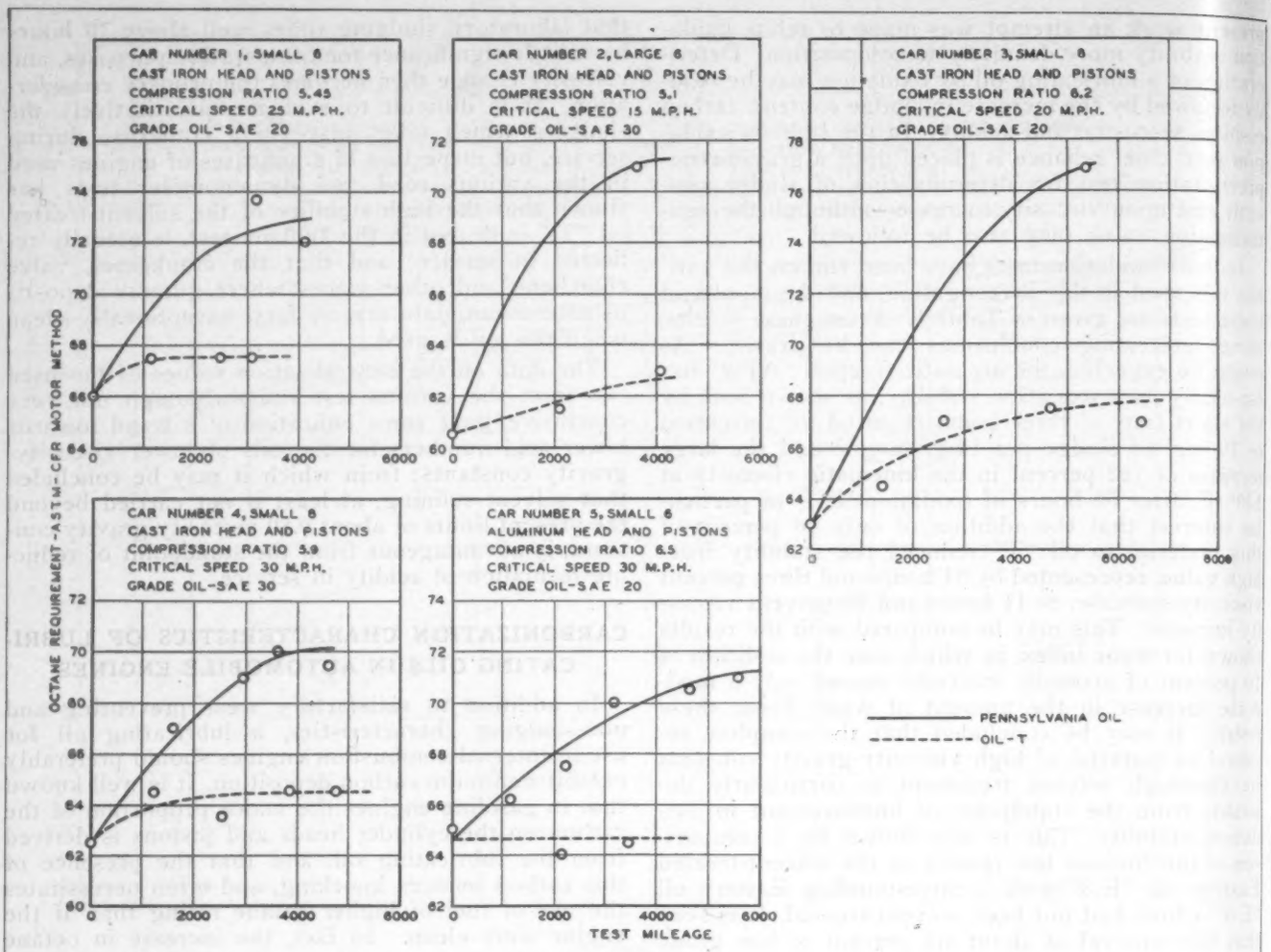

FIGURE 5

Effect of Oil Carbonization on Octane Requirement of Various Passenger Cars.

sylvania oil in each crankcase was replaced with the solvent-treated oil "T" and operation continued. The purpose of these tests was to investigate whether the use of this oil would in the course of time remove carbon deposits already accumulated.

The experimental procedure employed in the investigation of carbon formation consisted briefly of testing each car at intervals of about 1000 miles for detonating characteristics, using a number of gasolines of different octane rating (standard reference fuel "A-3" plus ethyl fluid). With each gasoline, the speed at which the knock disappeared on acceleration was determined as the upper incipient knock point; also the speeds at which the knock appeared (lower incipient knock point) and at which it reached a maximum intensity were noted. Care was exercised in testing to insure reasonably constant conditions of atmospheric temperature and humidity. Carburetion, manifold heating, and jacket temperatures were also kept as nearly constant as possible. Particular attention was paid to ignition timing, both as regards initial distributor setting and proper functioning of the advancing and retarding mechanism. At the beginning of the investigation, the ignition timing of each car was set according to factory recommendations, and the timing was noted to within half a degree of crankshaft rotation. At each subsequent test period, care was taken to check the ignition timing and to adjust it to exactly the initial setting, if necessary. All detonation testing was done on a 10 percent grade under full-throttle operation.

Differences in detonation characteristics resulting from use of the two types of oil were determined by comparing the octane requirements of each car at its critical speed, defined as the speed at which the maximum knock occurs when using a gasoline which knocks only slightly. This speed approximates that at which the curves of speeds for upper incipient knock, maximum knock, and lower incipient knock versus octane number converge. Although varying considerably between cars, this speed has been found to remain fairly constant for each car during continued operation. The octane requirement at this speed was read from a curve obtained by plotting speed at upper incipient knock versus octane-number requirement.

Figure 5 has been constructed as a summary of the data for typical cars showing the increase in octane requirement with mileage run on the respective oils. Inspection of the figure shows a very large difference in the carbon-forming properties of the Pennsylvania oils and the solvent-treated oil. It will be noted that, in the case of the engines having cast iron cylinder heads and pistons, the rate of increase in octane number with the Pennsylvania oils is about one point for each 300 to 400 miles driven—until the octane requirement has increased 7 to 14 points; whereas with oil "T" the rate of increase and the

total increase are only a fraction of these respective amounts. It is apparent that with the Pennsylvania oils the increase in detonation in about 4000 miles was sufficient to require a change to gasoline at least one commercial grade higher—and in some cases two grades higher—if the spark setting is to be held constant. With oil "T", the increase in detonation was so much less that a change in commercial grade of gasoline over the period of test was not required.

It is of interest to point out the effect of the aluminum cylinder head and pistons in car No. 5. From observation of this and other makes of cars having aluminum heads and pistons, it appears that, when the combustion chambers are clean, there is little difference between cast iron and aluminum construction in the octane requirements under strictly-comparable conditions—but that the aluminum construction is less susceptible to carbon accumulation. No discernible change in octane requirement was noted in the test with the highly solvent-treated oil in the engine equipped with an aluminum head, although some increase in octane requirement did occur in this engine with the Pennsylvania oil.

Figure 6 shows the effect of highly solvent-treated oil in removing carbon deposits previously accumulated by operation on Pennsylvania oil. It will be observed that in each instance the use of oil "T" caused a noticeable reduction in octane requirement; and it is believed that, upon continued service with the latter grade of oil, the octane requirement would approach asymptotically the equilibrium value obtained by the continued use of oil "T" in an initially clean engine.

The present investigation of carbon deposition has been concerned principally with an experimental determination of the effect of two general types of oils on octane requirements, but it is believed that a gen-

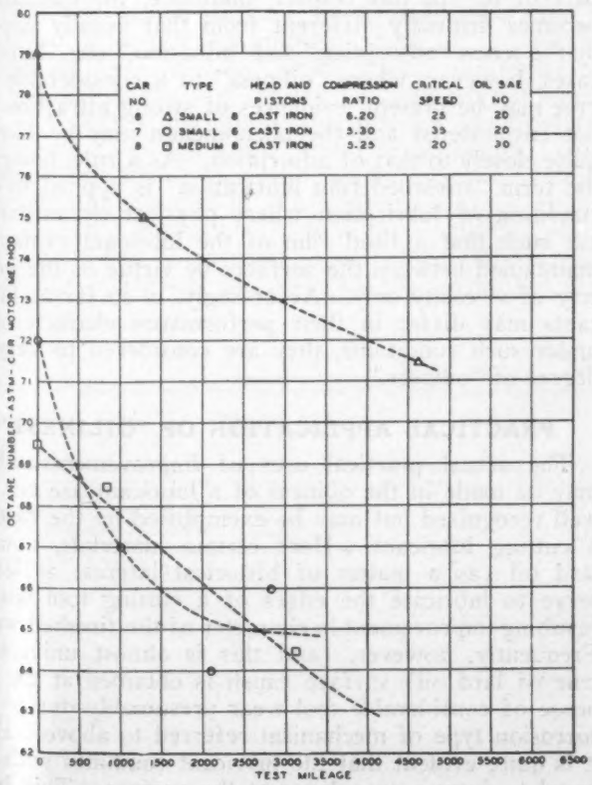
CAR NO
TYPE
HEAD AND PISTONS
COMPRESSION RATIO
CRITICAL SPEED
OIL SAE NO
6 △ SMALL 8 CAST IRON 6.20 25 20
7 ○ SMALL 6 CAST IRON 5.30 35 20
8 □ MEDIUM 8 CAST IRON 5.25 20 20
OCTANE NUMBER - ASTM - CFR MOTOR METHOD
TEST MILEAGE

FIGURE 6

Reduction in Octane Requirements by Running on Oil "T" After Carbon Had Been Deposited from Pennsylvania Oil.

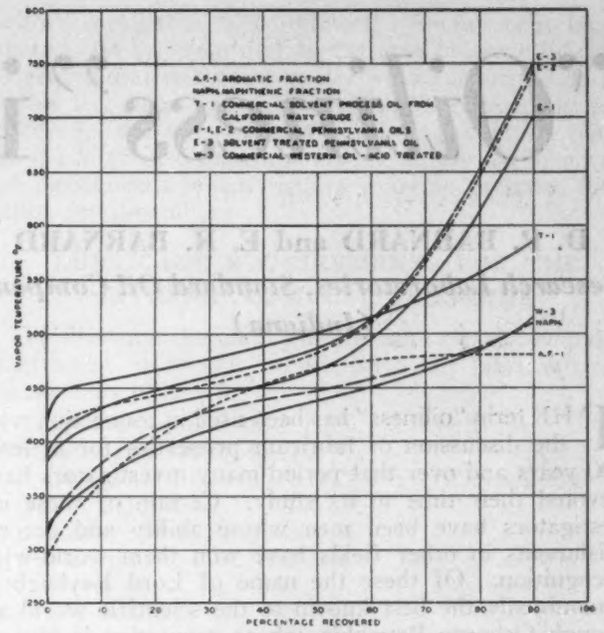
A.F-1 AROMATIC FRACTION
NAPH. NAPHTHENIC FRACTION
T-1 COMMERCIAL SOLVENT PROCESS OIL FROM CALIFORNIA WAXY CRUDE OIL
E-1, E-2 COMMERCIAL PENNSYLVANIA OILS
E-3 SOLVENT TREATED PENNSYLVANIA OIL
W-3 COMMERCIAL WESTERN OIL - ACID TREATED
VAPOR TEMPERATURE °F
PERCENTAGE RECOVERED

FIGURE 7

Distillation Tests at 1 Mm. Absolute Pressure.

eral discussion of the known factors in carbon formation may be of interest. The Conradson carbon residue test has had rather wide acceptance as a method for predicting the tendency of an oil to deposit carbon in the combustion chamber, although Bahlke and coworkers[10] have developed a relationship between carbon deposition and the 90 percent distilled point in a distillation of an absolute pressure of 1 mm. of mercury. This temperature they designate as the "carbonization index." The present investigation did not include a sufficient variety of oils to permit a conclusion to be drawn as to the relative value of the two tests. The solvent-process oil produced from distillates, oil "T," which was found to have a very low carbonizing tendency in service, has both a low carbon residue and a low carbonization index; while the Pennsylvania oils show much higher values in both of these tests. Data on these two tests for typical samples of the two varieties of oils are included in Table 1, and the distillation characteristics are also shown in Figure 7.

From a comparison of carbonizing tendency with composition, it appears that the tendency of an oil to deposit carbon in the engine is influenced principally by the content of two types of materials; viz., high-boiling, high-molecular-weight components which evaporate so slowly in the combustion chamber that decomposition occurs even though they may be highly paraffinic in character, and non-paraffinic compounds which tend to decompose even though they may not be especially high-boiling. In general, production of an oil as a distillate serves to eliminate the very high-boiling components, and solvent extraction either before or after distillation is effective in eliminating the unstable materials of low paraffinity. In operation on residual stocks, a simple solvent extraction will accomplish some reduction in carbon-forming tendency by removal of the compounds of low paraffinicity, but this process does not remove those high-boiling components which are of high paraffinicity. By solvent extraction in the presence of propane, however, a much greater reduction in carbon residue is obtainable[11] through the ten-

(Continued on page 328)

"Oiliness" in Motor Oils

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THE term "oiliness" has been used in connection with the discussion of lubricant properties for at least 100 years and over that period many investigators have devoted their time to its study. Certain of these investigators have been men whose ability and accomplishments in other fields have won them world-wide recognition. Of these the name of Lord Rayleigh is undoubtedly the best known to the scientific world although Osborne Reynolds, whose reputation is also of international magnitude, has devoted a very considerable amount of effort to the study of lubricant properties. In general the subject of lubrication, and particularly the phrase referred to as "oiliness," has been given much consideration by many including men of the highest scientific attainments but in spite of the talents which have been expended on this subject, relatively little concrete knowledge of it has been developed. In fact, there exists virtually no definition of this property except one or two attempts at description without an understanding of the mechanism. Some time ago one of the present authors collaborated in the preparation of a paper[1] in which this property was described as follows:

"The oiliness of a lubricant may be defined as the property by virtue of which one fluid gives lower coefficients of friction (generally at slow speeds or high loads) than another fluid of the same viscosity." In this case it will be noted that "oiliness" has been defined largely as a factor of ignorance. In attempting to obtain a clear understanding of the various terms used to describe this rather elusive property one very quickly finds himself chasing around in a circle, having arrived almost exactly nowhere as far as obtaining a clear-cut definition of "oiliness" is concerned. This lack of a satisfactory definition is occasioned, of course, by a dearth of information which might shed scientific light upon the exact nature of the property, and has given rise to the inevitable confusion resulting from the fact that an individual faced with the necessity of working with lubricants, and particularly in their manufacture and sale, is virtually forced to create his own definition and his own picture of this particular property. The situation is almost exactly as implied in the definition cited above. Everyone who clearly understands the significance of the term "viscosity" must recognize that the materials commonly used as lubricants possess properties apparent under certain conditions, inexplainable in terms of viscosity, gravity or any other recognized physical term. It is not surprising, therefore, that not only the technical but also the trade world should contain many evidences of personal opinions frequently of such nature as to appear rather whimsical.

There is a certain amount of agreement in that the word "oiliness" is generally accepted as implying reduction in friction between two metal surfaces obtained through the medium of some more or less mysterious property in which one oil may be considered superior to another. Probably the prevailing point of view is that "oiliness" is due to a weak chemical union between the oil (or certain constituents in it) and the metallic surfaces. The term "adsorption" probably comes nearest to describing it although the phenomenon undoubtedly differs quite radically from that implied when discussing such mechanisms as the adsorption of gases on solid surfaces or the concentration of active surfaces of substances which may be present in a solution only in a very high state of dilution. In certain instances, at least, it would appear that "oiliness" is due to a true chemical union and might even be termed as a form of very mild corrosive attack. This appears to be true particularly in the case of fatty acids or other materials containing relatively strong polar groups. Where such materials as these are used it is quite impossible to rejuvenate a metal surface without actually removing a part of it. In this respect, therefore, the mechanism becomes distinctly different from that usually implied by the terms "adsorption" and "adhesion," etc. In other cases, however, where "oiliness" to a considerable degree may be present, evidences of strong attraction are not encountered and the phenomenon may be likened quite closely to that of adsorption. As a rule, however, the term "adsorbed film lubrication" is applied to any condition of lubrication where physical circumstances are such that a fluid film of the lubricant cannot be maintained between the surfaces by virtue of the property of viscosity only. Accordingly, in so far as lubricants may differ in their performance characteristics under such conditions, they are considered to vary in degree of "oiliness."

PRACTICAL APPLICATION OF "OILINESS"

The actual practical uses of improvements which may be made in the oiliness of a lubricant are not too well recognized but may be exemplified by the case of a cutting lubricant. Here certain materials, notably lard oil (as a matter of historical interest at least) serve to lubricate the edges of a cutting tool with a resulting improvement in character of the finished work. Frequently, however, (and this is almost universally true of lard oil) surface finish is obtained at the expense of considerable tool wear presumably due to the corrosion type of mechanism referred to above. Here it is quite evident that the lubricant combines with the metal to form a soap layer at the surface. This layer is preferentially removed so that scratching of the surface or seizure between the tool and work surfaces are avoided. Removal of the soap film, however, leaves a

fresh metal surface which is immediately attacked by more lubricant. The net result is that under certain circumstances apparent surface wear may be increased many times over that which would be obtained with a lubricant relatively deficient in oiliness. Whereas the use of "oily" lubricants in such operations as those of metal cutting, drawing, etc., are fairly well recognized and their merits reasonably clear cut, attempts to apply this property to the lubrication of many mechanisms do not appear to be so well justified. Truly definite indications of advantages is a motor oil containing material designed to increase oiliness have been observed in the lubrication of the engine of the famous Ford Model T. Here lubrication of the friction bands of the planetary transmission and the service brake were accomplished by the motor oil. Relative slipping of these parts was under substantially static or seizing conditions with the result that chattering and general harshness in operation could be avoided through the medium of a compounded lubricant (an advantage which was frequently obtained at the expense of braking effectiveness), but there was never any evidence that engine lubrication or performance were affected by the presence of compounding material. No conclusive evidence of the beneficial effects of the addition of oiliness agents has yet been published.

In this discussion it should be recognized that the so-called "extreme pressure" lubricants are not in any way involved. The requirements for such lubricants differ radically from the properties implied by the term "oiliness." The purpose of the extreme pressure lubricant is to make possible the momentary carrying of rubbing loads far beyond the normal capacity of the surfaces. Reduction in friction *per se* is of little or no importance just so long as actual seizure and damage of the surfaces is prevented. In fact, some of the most effective extreme pressure lubricants would not be judged favorably by any of the methods which have been used in the past for evaluating oiliness. Again E. P. service conditions, have, as far as is known, no counterpart in the internal combustion engine. By and large it would not be expected that any of the methods employed for appraising E. P. lubricants would be applicable to the prediction of engine lubricating oil performance. Probably the only portion of the mechanism of an engine having even a partial approach to the conditions which require the use of extreme pressure materials in gear lubrication occurs at the point of contact of the cam with a mushroom type follower. As far as is known there is no evidence that an extreme pressure lubricant is required at this point in any workable engine design. Table I contains values for rubbing speeds, loads, temperatures and rates of frictional heat generation typical of the internal combustion engine on the one hand and of mechanisms which require extreme pressure lubricants on the other.

LUBRICANT REQUIREMENTS FOR THE INTERNAL COMBUSTION ENGINE

To illustrate the point a trifle more clearly, boundary coefficients of kinetic friction for a few lubricants may be taken as follows:

Orthodox motor oil	Coeff.	= 0.11
Synthetic motor oil	"	= 0.12
Castor oil	"	= 0.08
No. 1 Lard oil	"	= 0.06
Sulfurized E.P. Lubricant	"	= 0.09
Chlorinated E.P. Lubricant	"	= 0.08
Glycerine	"	= 0.05
Dry surfaces (no lubricant)	"	= 0.30
Sulfur-Chloride E.P. Lubricant	"	= 0.08

The above figures are typical of those obtained from rubbing on fully generated steel surfaces at rubbing speeds of about 50 feet per minute under pressures ranging from 5000 to 20,000 pounds per square inch. It is obvious that such coefficients do not prevail in the internal combustion engine, for if they did the losses from piston ring friction alone in a six cylinder engine of 100 indicated horsepower at 3000 r.p.m. would be in the order of 25 horsepower, which of course, is exorbitant.

Even at the period of high combustion pressures (when the piston is virtually at rest) there does not seem to be a chance for "oiliness" to have an appreciable effect—an observation which has been verified by actual experience. It has been reported that—particularly abroad—the use of unorthodox oils has made possible some very outstanding service performances with engines in airline operation. Here, however, the reports do not, by any means, indicate that "oiliness" can be considered the explanation. It is suspected, rather, that the effects of these materials on *sludge deposition* is the more likely explanation.

Typical examples of the authors' experiences with

TABLE I

MECHANISM	Max. Total Lead (Lb.)	Max. Unit Press. Lb./Sq. In.	Corres. Rubbing Speed Ft./Min.	Max. Oper. Temp. °F.	Rate of Heat Generation B.t.u./Min.
Hypoid Gear (100 H.P. Car)	6,500	8,700*	350	250	264
Worm Drive (100 H.P. Truck)	13,500	6,800*	425	300	663
Worm Drive (100 H.P. Tractor)	31,800	9,100*	205	300	753
Worm Drive Hoisting Gear	80,000	7,200*	195	200	1,800
Automobile Engine					
Cam and Follower	1,500	**	375	250	12
Main Bearing	1,600	400	2,000	275	8
Crank Pin	3,350	900	2,000	275	17
Top Piston Ring	425	310	2,500	400	5.5
Diesel Engine					
Cam and Follower	2,250	**	170	250	8
Main Bearing	5,200	740	1,180	275	16
Crank Pin	7,600	1,080	1,180	275	23
Top Piston Ring	1,180	410	1,500	500	9
Aircraft Engine					
Cam and Follower	4,950	(1)	2,360(2)	200	25
Main Bearing	6,350	1,060	1,300	200	21
Crank Pin (Master Rod)	10,400	1,260	1,300	225	35
Top Piston Rings	1,510	400	1,700	500	13

*Pressures for fully generated tooth.
**Line contact.
(1)Line contact roller type follower.
(2)Linear rolling speed of cam follower.

oiliness in the lubrication of automotive internal combustion engines are summed up in Table II, in which it is not apparent that there is any effect to be ascribed to the presence (or absence) of "oiliness" unless this effect is very slight or involves some mechanism hitherto unappreciated. This statement is made in spite of some very striking observations of improved aircraft engine cylinder lubrication, apparently through the "oiliness" route.

TABLE II

OIL	Static Coef.	Service	Comments on Lubrication
Non-Chatter Comp. Motor Oil	0.09	Model T Fords	No effect in engine proper relative to uncompounded oil.
Non-Chatter Comp. Motor Oil	0.09	Buick car	No noticeable effect on operation or life.
Castor Oil	0.11	Oldsmobile car	Gummy, varnish-like deposits in crank-case system
Orthodox Motor Oil	0.18	Passenger car engine	No difference in
"High Film Strength" Motor Oil	0.16	Passenger car engine.	Ring scuffing.
Penn Aircraft Engine Oils	0.18	Aviation engine.	Loss wear with Symthetic Oil
Synthetic Oil	0.22		

Virtually all instances of abnormal wear in automobile engines appear to be traceable to one or both of two causes (a) deficient oil supply and (b) presence of dirt or other abrasive material. In general it appears that the property of prime importance in determining the use of a motor oil is its viscosity and that all other properties should be judged either in the light of their effects on viscosity (and its maintenance in service) or by their secondary effects which may or may not be desirable. For example, a minimum change in viscosity with temperature is desirable as is also non-separation of wax. An oil should be as resistant as possible to oxidation and polymerization with their attendant influences which in general increase the viscosity of the lubricant and undesirably affect temperature characteristics. Changes in viscosity may result from volatility changes (not necessarily indicated by flash point) through loss of lighter constituents. It would seem from this standpoint that oils of low volatility would be desirable which would be true if it were not for the fact that such oils have been found generally to exhibit tendencies toward increased deposition of combustion chamber carbon.[2] Resistance to the formation of emulsions, particularly of the stable variety, is another desirable property which tends to insure pumpability of the oil. As secondary or undesirable effects which may occur as the result of failure of an oil to possess the properties given above, the following are cited. Oxidation may be responsible for large increases in viscosity, deposition of insoluble resinous material which tend to clog filters, oil screens, etc., and the formation of acidic material which may in turn corrosively attack bearing metals and wearing surfaces. There is some reason to believe, also, that sticking of piston rings in their grooves may be attributable in part at least to oxidation or a product therefrom. Excessive formation of combustion chamber carbon is also undesirable. The above represent most of the characteristics which may most profoundly affect the performance of a lubricant and the engine it is intended to protect.

The use of oil as an internal engine coolant, and similar auxiliary uses, does not play a part in this discussion as presumably those results could be achieved with water or some other fluid if viscosity and chemical inertness toward engine structural materials were not important. Within the scope of this discussion it appears that motor oil characteristics should be evaluated in terms of the foregoing outline. Discussion producing evidence to the contrary will be greatly welcomed. However, to round out further the author's present point of view on the role of oiliness in motor oils the following discussin of methods which have been employed for studying this property is submitted.

"METHODS OF INVESTIGATING 'OILINESS'"

From an historical point of view the so-called "static-friction" method of testing is probably the most important. In its simplest form this test is exemplified by a weight placed upon a plane surface which may be inclined to produce slipping. It is generally assumed that if one lubricant will permit the weight to slip at a smaller angle to the horizontal than may be required by another lubricant it may be taken as having the advantage as far as oiliness is concerned. Lord Rayleigh's[3] investigations involved the use of glass planes with bottles of various sizes and weights. It was with this simple apparatus that he verified the fact that under conditions of adsorbed film lubrication the coefficient of friction is independent of load. Subsequently Hardy[4] and his coworkers employed the same general scheme with many modifications and refinements such as working under special atmospheric conditions, at high temperatures, etc. One of the present authors[1] also employed the inclined plane method for some early experiments. As far as information is available, however, there is no indication either that the inclined plane static friction method is workable as a test procedure or that the results that may be obtained with it have any direct counterparts in service. The elaborate precautions and extremes as to manipulation, etc., which have been resorted to by those who have attempted to use this method would appear to offer considerable discouragement to any serious attempt to evolve a test procedure on such a basis.

One of the manipulative difficulties with the inclined plane consists in the virtual impossibility of reproduction of surface conditions from test to test. Several investigators[5–6–7] have attempted to avoid these difficulties by the use of rotating devices which presumably would generate their own contact surfaces. Here the general procedure followed has consisted in running in the surfaces, making an observation or two, and then allowing them to run in further before continuing. The machine of Deeley[4] or its modification has been employed most generally in recent years although to the best of the writer's knowledge it has shown no promise of developing into anything approaching a workable appraisal method.

As two surfaces not in relative motion, but on the verge of slipping, represent conditions of instability the erratic behavior of the static friction device is really only as would be anticipated. Therefore, several investigators have attempted to avoid static friction measurements and to substitute for them observations made at very low speeds and occasionally under very heavy loads. The Deeley machine has been used in this manner as have also some of the older devices of Thurston, Riehle, Hopps, Smith, Martens, Stanton, Daimler-Lanchester, Herschel, etc.[5–6–7] Again, none of these schemes have ever appeared promising as a test procedure, nor indicated that the results which might be obtained would have any particular significance as far as predicting service operations is concerned. Of the various dynamic machines which have been employed, two devices of Kingsbury deserve special mention. First, Kingsbury's

small spindle machine might be considered the forerunner, as far as its physical form is concerned, of the General Motors and Almen extreme pressure testing machines. Second, his classical tapered plug experiments would appear to throw rather interesting light upon one current attempt at devising an appraisal method.

In addition to the various forms of friction devices several attempts have been made to evaluate oiliness indirectly through the medium of devices aimed at the measurement of surface tension, film thickness, evidence of adsorption, etc. However, no very important results from such devices have been realized as would be expected from the fact that the actual nature of the term "oiliness" is so poorly understood. Therefore, attempts to apply such indirect procedures could represent nothing more than blind guesses. It would seem that this is particularly true of the attempts to measure the thickness or mass of an oil film adhering to a metal surface. Except as to give some slight indication of minimum possible thickness (i.e., the thickness of a monomolecular film) it would be quite unreasonable to expect that the film which might repose upon the exposed solid surface of a piece of metal would have any direct relation to either thickness or the ability of film to adhere to surfaces undergoing relative rubbing contact.

Once again the foregoing criticism of the devices intended for the appraisal of "oiliness" should not be considered as having any relation to those evolved for the rating of extreme pressure lubricants. So far as the authors are aware the history of this latter subject can be written in terms of the following test devices:

1. Actual gear set as employed by Gleason.
2. First General Motors machine.
3. Almen machine.
4. General Motors ball bearing test device.
5. Timken machine.
6. Floyd machine.
7. Bureau of Standards machine.
8. S.A.E. machine (now being developed).

From Table III it will be noted from the operating conditions incorporated in the design of these machines that there is no particular similarity between the duty which may be imposed upon a lubricant when subjected to e. p. tests and the requirements of the internal combustion engine. In general it would not appear that motor oils could be rated with these devices with the assurance that the results would have any significance as far as performance in an internal combustion engine is concerned even if concrete evidence of oiliness effects existed.

Another device consists of a mechanism for revolving a metal ring at a fairly high speed. The principle involved consists in weighing the metal ring before a lubricant is applied to its surface and then determining the increase in weight resulting after it has been "whizzed" for a length of time, (presumably sufficient to discharge all of the lubricant except a film which would adhere even between rubbing surfaces.) If one were to refer to the early work of Rayleigh[3] and subsequently that of Langmuir [8] he would come to the conclusion that the films which might well serve to effect profoundly the friction characteristics of surfaces could be quite thin indeed. Langmuir's work indicated that lubricants will ordinarily tend to spread over surfaces until a monomolecular film is formed. Such films are in the order of 10^{-7}cm. thick. Rayleigh's work indicated that the thickness of an adsorbed lubricant film need not exceed 0.0000004 inch. Even the classical tapered plug experiments of Kingsbury indicate no effect other than those of simple viscosity at films as thin as .00025 inch. Obviously if the film in a running bearing could be as thin as this and at the same time show evidences of viscosity characteristics alone, an adsorbed lubricating film layer would need only to be quite thin indeed. In fact, due to the fourth power effect of the hydraulic radius upon viscous flow characteristics, it would be expected that a boundary layer could never amount in thickness to more than a very few percent of the total passage space involved without its presence becoming manifest. On the basis of such evidence, it would seem that even if a centrifuge could be devised which would discharge all except the truly adsorbed boundary layer of lubricant it would be virtually impossible to detect the presence of the remaining layer by any scheme of weighing.

For example, the molecular length of oleic acid is about 1.1×10^{-7} cm. according to Langmuir[8], and the density is 0.894. Assuming thorough molecular coverage, which actually does not occur, the increase in weight for a solid body from molecular coverage would be 9.84×10^{-8} grams per square centimeter of surface. If Rayleigh, Deeley, Hardy, Tower, Langmuir, Kingsbury, et al are to be taken as authority, the thickness of the boundary or "greasy" layer as in the order of 4.0×10^{-7} inch, or from five to 10 molecules thick at most.[2] Then, to measure oiliness with any type of centrifuge which is designed to throw off all but the boundary layer it will be necessary to determine precisely an increase in weight of 9.84×10^{-7} grams per square centimeter of metal surface exposed. If the rotating band or disc of such a machine had an area of 100 square centimeters, the total increase in weight from the boundary film would be 9.8×10^{-5} grams or 0.098 milligram, a very difficult quantity to weigh precisely. Inasmuch as the best evidence points to even thinner films or layers under boundary conditions, it is difficult to conceive a centrifuge that will definitely indicate the presence of oily or active material. Added to this fact is the very decided uncertainty as to the relation between the weight of any such film and the properties of the lubricant in service in an internal combustion engine. Other devices have also been used some of which consist of arrangements for determining the friction characteristics of two rubbing surfaces. All such have the same fundamental difficulty in that no relation between either the condi-

TABLE III

Testing Machine	Max. Load (Lb.)	Max. Unit Press. Lb./Sq. In.	Rubbing Speed (Ft./ Min.)	Max. Oper. Temp. (°F.)	Rate of Heat Generation (Btu/Min.)
General Motors (a)...	25,000	25,000	130	700	460
Almen(b).....	1,900	15,000	75	300	20
Timken.....	900	20,000*	350–500	250	60
Bureau of Standards.	2,500	†	200–1400	500	280
S.A.E. Machine.....	6,000	†	200–1400	700	600

*Test pieces have virtually line contact at start of test. Wear on block increases bearing area to about 1/25 sq. in. during test.
†Line contact maintained throughout test. Unit pressures are extremely high and depend upon the elasticity of the metals.
(a)Large General Motors Machine.
(b)Small General Motors Machine.

tions which exist in the machine (or the results which may be obtained with it) and service performance are obtainable. It would seem that while a hundred years of virtual failure may be quite discouraging, continued effort should be directed toward establishing definite knowledge as to the mechanisms which may be involved in "oiliness" and in the development of an accurate and clear understanding of it and to determine what, if any significance it has in the case of motor oils.

CONCLUSION

As a recapitulation the authors submit the following summary:

1. Up to the present a definite explanation of the nature of "oiliness" has not been evolved even though its existence is recognized.
2. There is no clear-cut published evidence of effects beneficial or otherwise, of oiliness in the lubrication of the conventional internal combustion engine.
3. Extreme pressure lubricant test conditions have no close counterparts in the internal combustion engine.
4. Where effects due to adsorbed film, or "oily" lubrication are noted, the evidence indicates that these films are very thin—probably of molecular magnitude.
5. Direct measurements of the thickness or mass of such films are not practicable.

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Service Characteristics of Motor Oils As Related to Composition

(*Continued from page 323*)

dency of the propane to reject the highest molecular weight components. In fact, very low carbon residues may be obtained on residual stocks with the proper choice of selective solvents and propane ratio.

As another aspect of the effect of boiling range on the characteristics of lubricating oils, the relationship between boiling range and viscosity index is of interest. It is generally recognized that, for oils of a given viscosity and gravity, the wider the boiling range, the better the viscosity index. On the basis of viscosity index alone, the obvious choice would be to produce a wide-boiling residual oil. In practice, however, it is found that this involves a sacrifice in flash point and in carbon-forming tendencies. Since the present investigation has shown that well-treated distillate oils are not deficient in lubricating value, the restriction of boiling range in order to reduce carbon formation appears well justified.

From the data presented it is seen that the service characteristics of a solvent-treated oil from which both the highest boiling and the less paraffinic components have been completely removed are exceptionally good. The lubricating or wear preventing value of such oil is unexcelled by that of any of the oils examined; the oil has high oxidation stability; and, in addition, the carbon-forming tendencies are such that a definite improvement in gasoline performance is obtained. The advantages in minimizing the rate of wear of the engine are self-evident. The high oxidation stability is reflected in service in low tendency towards sludge formation or viscosity change. As affecting gasoline performance, the low carbon-forming tendency of such oil permits the use of higher compression ratios with accompanying improved performance, without necessitating frequent carbon removal or the eventual use of higher-octane fuel.

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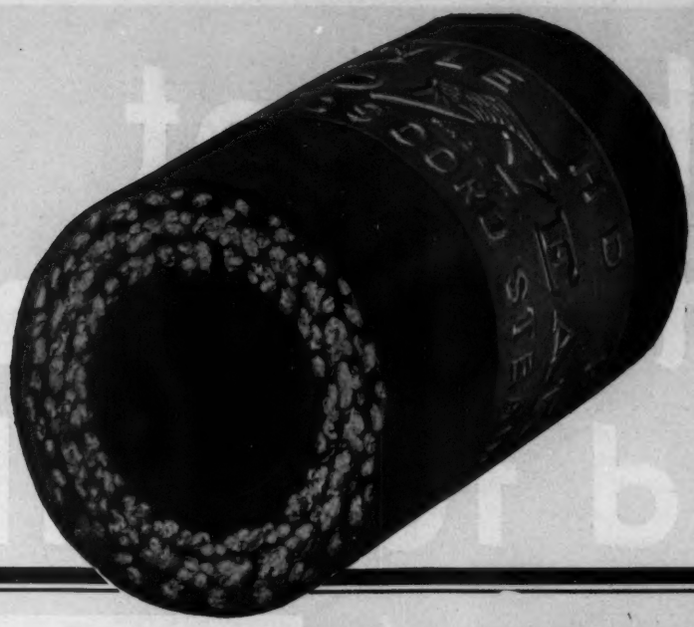

HE ENDED THEIR "STEAM HOSE BLUES"

A LARGE refinery in the mid-continent field was looking for steam hose that would stand the combination of high pressure and hot dry climate. They had tried countless brands, asbestos as well as ply construction, and discarded them one by one.

Then the G. T. M.—Goodyear Technical Man — arrived on the scene. He made his customary thorough analysis of operating conditions — recommended 1" Goodyear Style HD Asbestos Steam Hose — and persuaded the refinery to try out a few sample lengths in a comparative test.

Now, many months later, the refinery reports that the Goodyear hose shows practically no signs of wear or failure—while others in the test are *"about ready to throw in the sponge."* Needless to say, this plant is now equipping with Goodyear.

12 times stronger construction

Where hose failure means costly delay it pays to use Goodyear Style HD Asbestos Steam Hose. Its de luxe construction, employing highest quality asbestos cord carcass and specially compounded tube and cover, is up to 12 times stronger than ordinary hose—insuring much longer service under severest conditions.

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You will get the same money-saving service from Goodyear air hose, welding hose, water hose, drilling hose, oil suction and discharge hose. All are service-proved products of Goodyear's quarter-century of experience in reducing refining costs—all are individually specified to the job by the G.T.M.

Many refiners consult this practical expert on all hose problems—perhaps he could help you. Just write Goodyear, Akron, Ohio, or Los Angeles, California — or the nearest Goodyear Mechanical Rubber Goods Distributor.

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Why not settle it once and for all—

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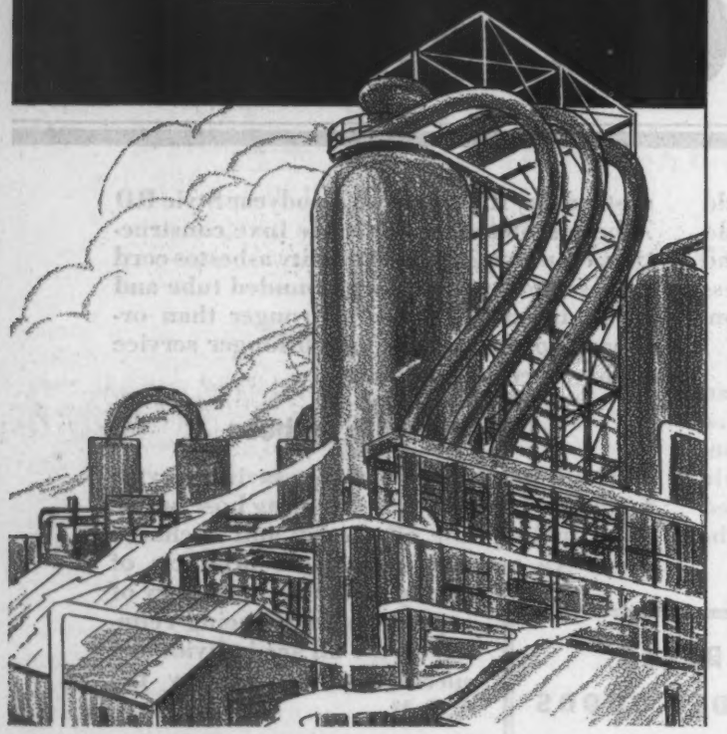

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NATIONAL U S S 18-8 Stainless and Heat Resisting Pipe and Tubes come in a wide range of diameters, wall-thicknesses, and lengths. They can be readily bent, welded, and otherwise fabricated. Produced with unrivaled facilities by the largest manufacturer of tubular products in the world, an organization that offers a complete piping service to the refining industry. NATIONAL engineers and metallurgists will be glad to give information as to the best application for any particular requirement. Descriptive literature sent on request.

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The Look Box

(*Continued from page 238*)

Bureau of Mines Activities To Be Expanded

AN APPROPRIATION of $1,970,311 to the Bureau of Mines for the new fiscal year beginning July 1 is made in the Interior Department supply bill which was recently signed by the President. This amount includes a net increase of approximately $600,000, granted in response to numerous appeals from the mining industry urging that the Bureau be given sufficient funds to resume many important services that had been discontinued or curtailed because of cuts in appropriations during past years, and to undertake important new work that lack of funds had hitherto prevented.

The additional funds will permit an expansion of the economic and statistical studies of the Bureau so as to give the mineral industry a complete picture of mineral resources, production, consumption, and trade conditions, as well as factors affecting the movement and utilization of mineral commodities. This information will also be extremely valuable to congressional committees, permanent agencies of the Federal Government and the like.

Investigations of health hazards in the mineral industries, which were suspended two years ago, will be resumed. This work includes studies of harmful dusts and gases and other causes of occupational diseases contracted by miners. Instruction in safety and first-aid, particularly at small-scale mining operations, can be extended. Such operations have attracted many inexperienced and unemployed men and as a rule do not provide means of avoiding dangers that may result in accident or ill health. Training in first-aid is one of the most effective ways of education in safety.

The Bureau will expand its studies on low-temperature carbonization of coal in the effort to find a solution for the smokeless-fuel problem and thus prevent waste of fuel value in the soot and tar composing the smoke and will avoid damage to buildings, clothing, etc.; to accelerate the development by the industry of commercial carbonizing processes; and to determine the composition of byproduct oils and tars and develop commercial uses for them. Apparatus on a small, laboratory scale will be constructed to study the extraction of motor fuel from coal and lignite as one step in research looking forward to the time when known reserves of petroleum will be exhausted and when a major oil-from-coal industry will be a national necessity.

Factual information with respect to production, storage, and utilization of petroleum and natural gas is in greater need by the government and the industry today than ever before. Reserves of these natural resources are limited and substitutes can be had only at high cost, so it is important that petroleum shall be produced without waste, as needed, and that as little oil as possible shall be left underground beyond recovery. To make the best production, exact engineering information is needed concerning conditions in underground reservoirs and wells, and as to the physical laws governing the flow of oil. Also new plans of proration, production control, and unit operation of newly developed structures are full of technical difficulties. Adequate studies to obtain the needed engineering information can be made only by an experienced and impartial organization such as the Bureau of Mines. The additional funds for the coming year will enable the Bureau to resume its activities in this field where its studies in the past have invariably been reflected in reduced costs, increased safety and efficiency, and conservation of resources.

Conventions

S. A. E. The Society of Automotive Engineers will hold its summer meeting at Greenbriar Inn, White Sulphur Springs, West Virginia, June 16 to 21.

A. S. C. E. The American Society of Chemical Engineers, holds its meeting in Cincinnati, Ohio, June 19-21.

P. G. C. O. A. Pennsylvania Grade Crude Oil Association plans to hold its annual convention at State College, Pennsylvania, June 20 and 21.

A. S. T. M. American Society for Testing Materials annual meeting is scheduled for June 24 to 28 at Detroit, Michigan.

A. C. S. The American Chemical Society meets at San Francisco, California, August 19 to 24.

N. P. A. The National Petroleum Association, September 25-27, will hold its annual meeting at Atlantic City.

N. S. C. National Safety Council holds the twenty-fourth annual Safety Congress, in Louisville, Kentucky, October 14-18.

A. P. I. The American Petroleum Institute will hold its 16th annual meeting at the Biltmore Hotel, Los Angeles, November 11-14.

C. N. G. A. The California Natural Gasoline Association holds its meeting the first Thursday of every month in the Richfield Building, Los Angeles, California.

Low Temperature Refining Process Licensed

STANDARD Oil Company of California has announced appointment of Stratford Development Corporation of Kansas City, Missouri, as exclusive licensing agent, in all countries, of its Low-Temperature Refining Process.

This process, covering the acid treatment of distillates at controlled, reduced temperatures, is to be offered to the petroleum industry, along with the Stratford quick-contact, contactor- centrifuge process, in one license, thus making possible the use of either process in any form or any combination of the two, best suited to any individual treating problem.

The economic soundness of these processes, particularly for the treatment of pressure distillates, has been amply proven by large-scale installations operating profitably over a period of several years. The benefits of this commercial operating experience together with the results of the extensive research which has been and is being carried on to further improve the processes will be made available to licensees through Stratford Development Corporation.

Development of the Low-Temperature Refining Process and its large commercial applications in the refineries of Standard Oil Company of California have been described in various publications, among which was a paper presented by R. A. Halloran at the meeting of the World Petroleum Congress, London, in 1933.

A large commercial application of the Stratford contactor-centrifuge process in the refinery of Continental Oil Company, Baltimore, Maryland, has been in satisfactory operation for several years, as described in various petroleum journals.

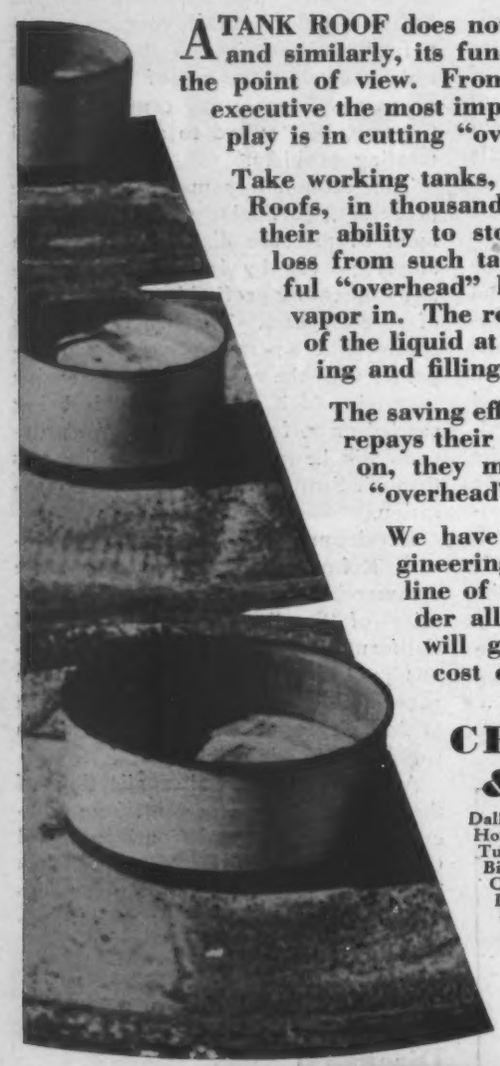
Diffusional Processes Discussed

CHEMICAL engineering problems connected with heat transfer and with the transfer of material from one phase to another were discussed May 10 by Professor Walter G. Whitman of the Massachusetts Institute of Technology at a joint meeting of the Society of Chemical Industry with the New York sections of the American Chemical Society, the Electrochemical Society and the Societe de Chimie Industrielle. The meeting was held at the Chemists' Club, 52 East 41st Street, New York, and was preceded by a dinner in honor of the speaker.

Professor Whitman's paper was entitled "Diffusional Processes." The transfer of material and of heat from one phase to

An "OVERHEAD" VIEW of WIGGINS PONTOON ROOFS

TANKS THAT STOP EVAPORATION LOSSES



A TANK ROOF does not look the same from all angles and similarly, its function may depend somewhat on the point of view. From the viewpoint of the refinery executive the most important function a tank roof may play is in cutting "overhead."

Take working tanks, for example. Wiggins Pontoon Roofs, in thousands of cases, have demonstrated their ability to stop the tremendous evaporation loss from such tanks. They eliminate this wasteful "overhead" by simply keeping air out and vapor in. The roof floats directly on the surface of the liquid at all levels, stopping both breathing and filling losses.

The saving effected by Wiggins Pontoon Roofs repays their cost in a short time. From then on, they make a substantial reduction in "overhead" throughout their life.

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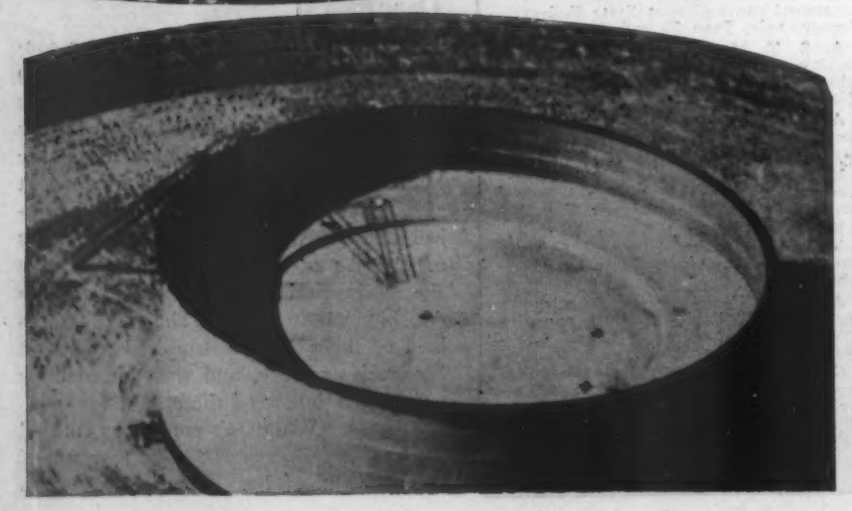


STOP EVAPORATION

another is largely a problem of diffusion through films at the fluid boundaries. Recent work has demonstrated, however, that mixing by turbulence within the main body of fluid is seldom so complete that non-uniformities can be disregarded. He cited numerous examples of transfer problems which are dominant in the practical operations of chemical industry. He showed that apparently diverse phenomena could be correlated by simple generalizations and emphasized the value of such correlations in the work of the chemist and chemical engineer.

Professor Whitman was formerly associate director of research of the Standard Oil Company (Indiana). Last fall he was appointed head of the Department of Chemical Engineering at the Massachusetts Institute of Technology. His outstanding scientific contributions have been in the fields of corrosion and the absorption of gases by liquids. His developments have contributed to increased efficiency in operation in various industries such as the recovery of gasoline from natural gas, the manufacture of liquid carbon dioxide and dry ice and the production of refrigerants for household use. He graduated from the Massachusetts Institute of Technology in 1917 and took his master's degree there in 1920. He joined the staff of Standard Oil Company (Indiana) in 1926 and was appointed associate director of research of that company in 1930.

Petroleum Industry One of Safest

DECLINES of 17 percent in the frequency of fatal injuries and of 11 percent in the severity of injuries gave the petroleum industry in 1934 one of the best accident prevention records to date, according to the final report for the year made by H. N. Blakeslee, director of the American Petroleum Institute's Department of Accident Prevention.

Adjustment of forces, addition of men, and problems of supervision under NRA working schedules led to an increase of 10 percent in frequency of injuries, but the industry's frequency rate of 14.31 injuries per 1,000,000 hours worked was less than the 1933 all-industry frequency rate of 14.56 and probably less than the 1934 all-industry rate, data for which are not yet available. The National Safety Council has forecast a large increase in the all-industry rate.

It is expected that the petroleum industry's accident severity rate, 1.69 days lost for each 1000 hours worked, also will be below the all-industry 1934 rate.

Blakeslee's records show that between 1927 and 1934 the petroleum industry, through practical accident - prevention measures, has reduced its accident fre-

quency rate from 31.15 injuries per 1,000,000 hours worked to 14.31 injuries. In the same period the accident severity rate has been cut from 2.65 days lost per 1000 hours worked to 1.69. During 1934 there was one lost-time injury to each 28 workers, as compared with one injury to each 11 workers in 1927. The number of fatalities was only one to each 2374 workers in 1934, as against one to each 1476 workers in 1927.

A.S.T.M. Annual Meeting in Detroit

IN order to provide ample time for the presentation of the many technical reports and papers which will be presented at the Thirty-eighth Annual Meeting of the A.S.T.M. to be held in the Book-Cadillac, Detroit, June 24-28, 16 sessions are scheduled. During the five days of the annual meeting, the society's third exhibit of testing apparatus and related equipment will be in progress. Latest developments in the testing and scientific instrument field will be on display and A.S.T.M. committees and research laboratories will also take part.

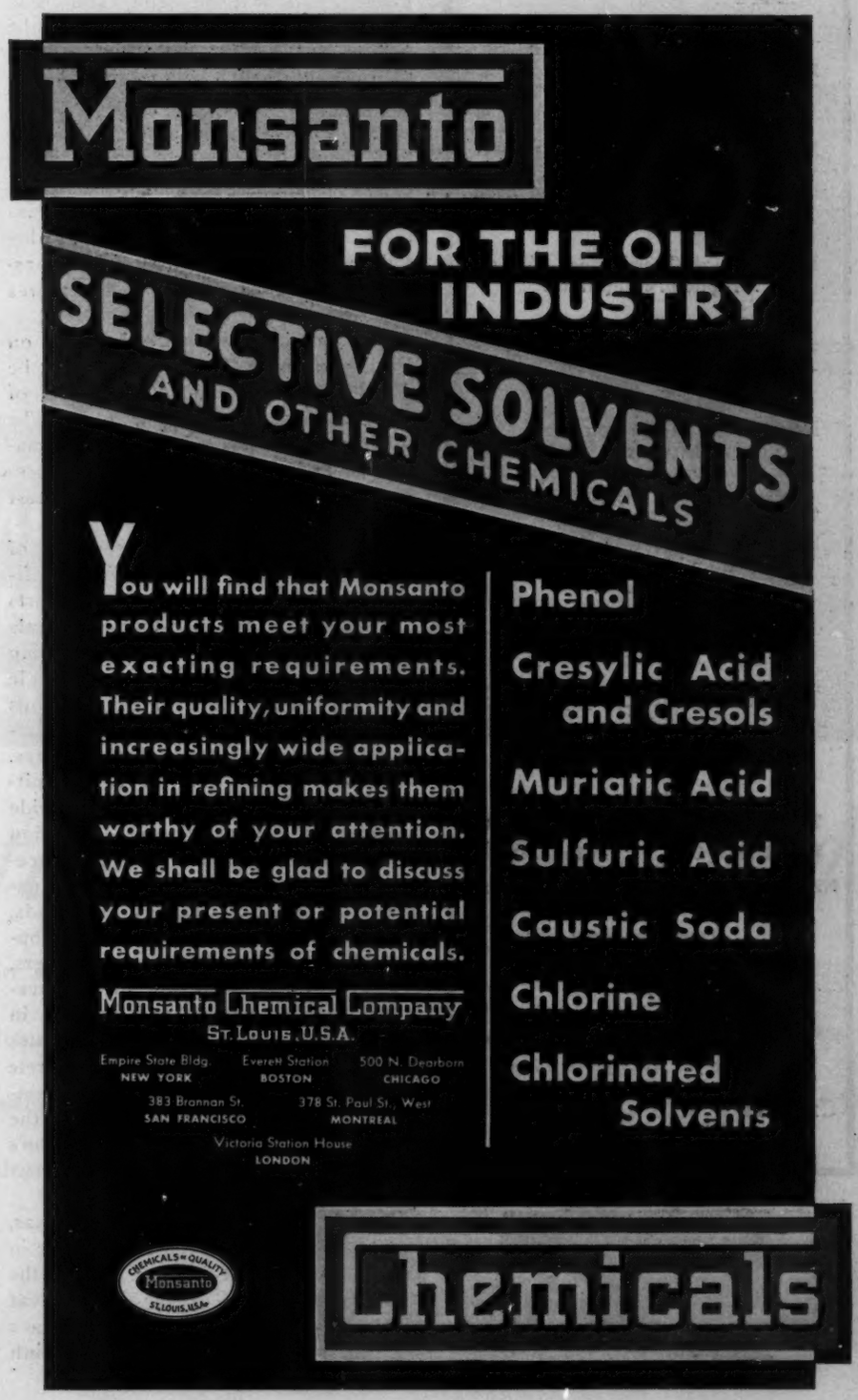
While Monday, June 24, will be devoted to meetings of many of the society committees, the annual meeting opens formally at 10 o'clock Tuesday morning with an address of outstanding interest by C. F. Hirshfeld, chief of research department, Detroit Edison Company, and the presentation of the president's address by Doctor von Schrenk, to be followed by the report of the executive committee and introduction of the new officers.

The Tuesday afternoon meeting will comprise a session on testing, including papers on elastic strength and its determination, hardness testing of light metals and alloys, relation between tension, static and dynamic tests and description of a new method for dynamic hardness testing.

A session of unusually wide interest, held on Tuesday evening is to be devoted to a symposium on the "Place of Materials in Automobile Roads and Rides" which will stress the important part that materials play in automobile roads and rides, a discussion of the problems relating to materials in this field and an indication of further advances which appear to be desirable and which the future may reasonably hold.

Simultaneous sessions are scheduled for Wednesday morning, one being devoted to ferrous materials, the other to paints, naval stores and timber. In addition to committee reports, the session on ferrous metals will include papers on the endurance testing of rear axle gears and gear steels and the effect on elastic properties of heavy steel plate of cold bending and stress relief. In the session covering timber one paper will discuss methods of testing fire-retardant treated wood, while another is devoted to distribution and variations of properties of southern pine wood. The session on Wednesday afternoon devoted to rubber products and petroleum will include papers on the effect of volatility on oil consumption and on the influence of engine design on oil consumption.

The Edgar Marburg Lecture will be given Wednesday afternoon. Dr. L. B. Tuckerman of the National Bureau of Standards will deliver the lecture on "Aircraft: Materials and Testing." The annual A.S.T.M. dinner is to be held Wednesday evening and will be followed by two addresses on "The Relationship of Materials to the House of Today and Tomorrow." An official of the Federal Housing Administration will give the viewpoint of the government, and an outstanding authority on the subject of modern housing will deliver an illustrated lecture on what is being done in this country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and abroad to solve housing problems.

The two sessions on Thursday morning are devoted to corrosion and its related problems and coal and coke, textiles and electrical insulating materials. The paper in these sessions cover such subjects as control of corrosion in air conditioning equipment, corrosion tests of steel pipe, testing of wool by the microscope, etc.

On Thursday afternoon the annual golf tournament will be held and a number of excursions and industrial trips are planned. Sessions on Thursday evening are devoted, respectively, to fatigue and effect of temperature on metals, and waterproofing and road and paving materials. Papers in the first-named session cover tests on tin bronzes at elevated temperatures, creep characteristics of aluminum alloys, high speed fatigue tests on metals, and a fatigue machine for testing small diameter wire. In the other session there will be discussion of stability of granular mixtures, penetration method of measuring soil resistance, physical properties of asphaltic mixtures at low temperatures and others.

Two sessions will also be held on Friday morning. One of these will be devoted to spectrographic analysis of materials, steel, plainum, etc. The other will be devoted to ceramic materials and includes papers on prestressing ceramic beams, a wear test for flooring materials, etc.

One of the outstanding sessions of the meeting is to be held Friday afternoon, devoted to committee reports and papers in the non-ferrous metals field. Papers discuss the following subjects: making and testing single lead crystals; testing in the precious alloy field; present-day testing requirements in precious metal duplex alloys. A number of the non-ferrous committee reports will include data of wide interest and value. The other session on Friday afternoon is devoted to cement, clay pipe, etc., and includes papers on elastic caulking materials, measurement of particle size distribution by optical methods and others. The closing session on Friday evening includes papers and reports in the field of concrete. Papers discuss the chemistry and physics of concrete shrinkage, research on concrete disintegration, and determination of the modulus of elasticity and Poisson's ratio of concrete.

Barney Osborne, Gladewater, Texas, and associates started construction late in May on a four-unit gasoline plant in the Gladewater section of the East Texas field. Plant is on J. B. Sowell et al's W. P. Luse-E. L. Walker lease, near south bank of the Sabine River.

One Hundred Days; One Million Barrels

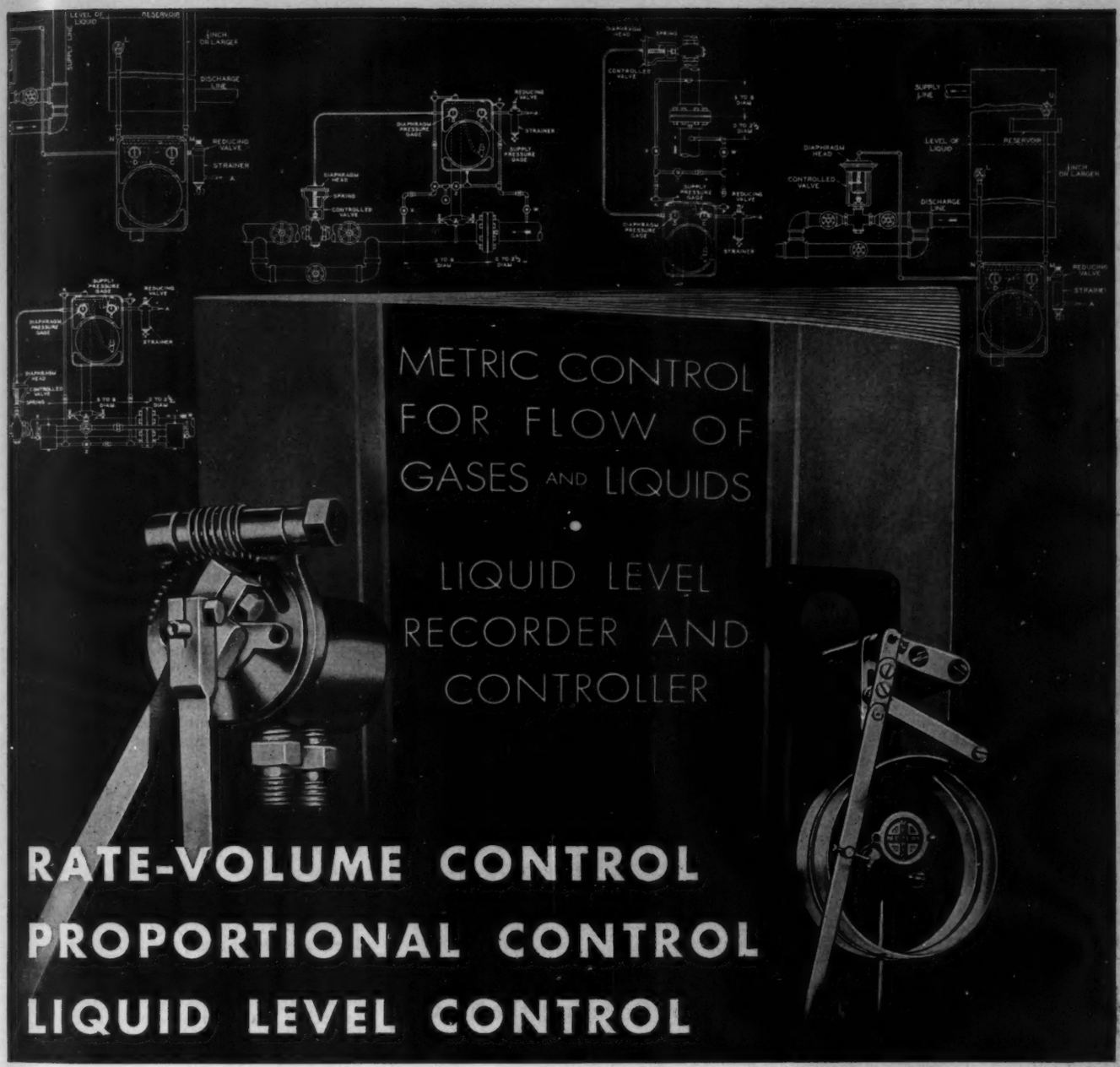
OPERATING on Kansas crude produced in the McPherson area, Globe Oil & Refining Company at McPherson, on May 19 completed 100 days of continuous operation, skimming and cracking in its Winkler-Koch combination unit. And on May 19 the plant was still going strong with every prospect of continuing operation until June 1 or longer. Press time for THE REFINER prevents inclusion of the final results for this run. On May 9, when the Editor of THE REFINER visited the plant, there was 91 days continuous operation behind the operating forces, and these men were on their toes and determined not only to keep the plant functioning efficiently at its rated capacity of 10,000 barrels daily, but also to complete that 100 days of operation and to pile up more days on top of that if possible.

During the past year while E. J. Mary has been in charge of operations at McPherson, certain changes in processing facilities and in method of operation have been put into effect. In regard to the recently completed record run "E. J." modestly gives all credit to an efficient and energetic crew of willing process operators. Each and every man on the plant, in addition to a determination to operate a plant safely (and to support an apparently unbeatable basket ball team), gives his best in the effort toward establishing a record for cracking unit operation on Kansas crude. On the other hand, there is a lot to be said about efficient and proper management of a refinery—and congratulations are herewith passed out to E. J. Mary.

On the one hundredth day total charge at the plant was 1,012,059 barrels, charging 39-42 gravity Kansas crude. This crude is corrosive, as those familiar with Kansas oils well know, and it does not hurt matters if a lot of common sense and precaution is exercised in operating on such an oil. The injection of a little lime solution is one means of prolonging equipment life and hours on stream.

During the 100 days reported combined Bunker "C" fuel oil and loss was 24.62 percent; the balance being overhead products. Due to a large rural trade in that territory which requires at least three types of white tractor fuels and one prime white distillate, and water white kerosene, it has been deemed inadvisable to operate for maximum yields of gasoline. However, the gasoline yield during the period of the run was 59.02 percent. About one half of this was cracked gasoline with an octane rating of about 65.

This plant was described in a special section in THE REFINER in August, 1933. Since that time a number of changes and



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certain additions have been made, adding to efficiency and therefore to the interest in this type of operation. A complete engineering type of article discussing results secured has been promised for early publication in THE REFINER.

W. B. SULLIVAN, well known in the development and manufacture of heat and corrosion resistant alloy castings, and organizer of the Michiana Products Corporation, has joined the Alloy Department of Lebanon Steel Foundry, located at Lebanon, Pennsylvania.

PLANT ACTIVITIES

Gasoline Plant: J. E. Crosbie, Inc., Tulsa, is to build a gasoline plant in NE 30-2-7e, in the Fitts Field, Southern Pontotoc County, Oklahoma. Location is on a lease owned by Magnolia Petroleum Company. Both absorption and compression will be used and some of the equipment will be moved in from a company plant in the Lovell field, Logan County, Oklahoma.

Refinery: Mongeau & Robert Company, Ltd., Montreal, Quebec, Canada, is reported planning erection of a $500,000 skimming plant on a site at Point-aux-Trembles.

Refinery: Pacific Oil Company, Montreal, Quebec, Canada, has secured an industrial site at Point-aux-Trembles, and is reported planning erection of a skimming and cracking plant at total cost of $3,000,000.

Purchase: John W. Gilliland, Keith Jones and associates have acquired the natural gasoline plant operated by Crescent Natural Gasoline Corporation, Overton, Texas. Plant, located near Kilgore, was originally erected by Tall Pines Natural Gasoline Corporation in 1934. New owners plan to install additional equipment and to connect about 600 more wells in northern Rusk County.

Sale: Jacks Petroleum & Refining Company, owning a 1000-barrel skimming plant near Gladewater, East Texas field, has been acquired by M. S. Johnson et al. The plant formerly was operated at the H. & M. Refining Company, Sabine Refining Company and Godlin Refining Company.

Sale: Arrow Refining & Producing Company, Overton, Texas, has sold its 5000-barrel skimming plant and 1000-barrel cracking plant to Gilliland Refining Company, headed by John W. Gilliland, Gladewater, Texas. Henry B. Mays, president of Arrow and substantial stockholder, has been retained as plant manager.

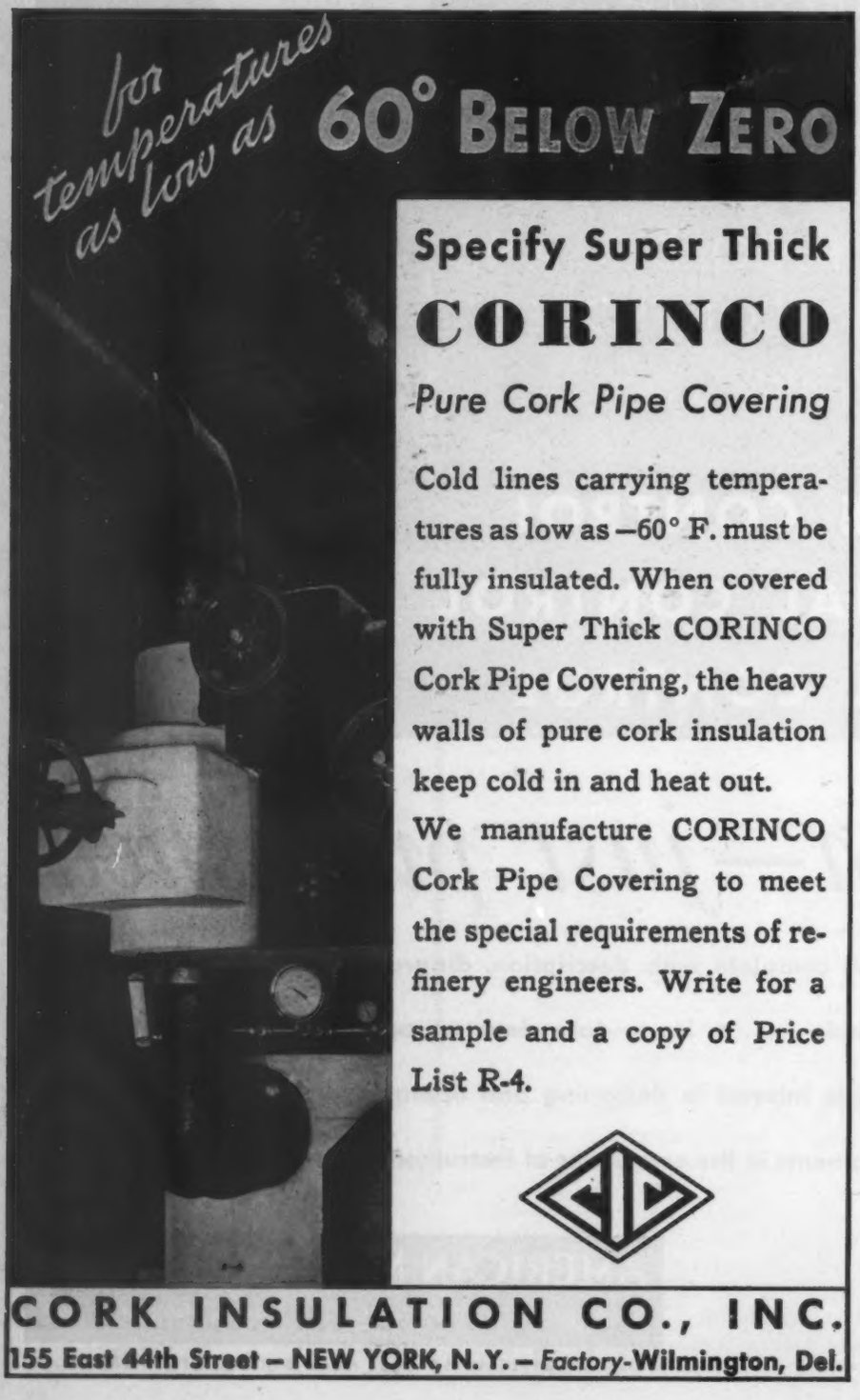
Refinery: Lakeland Refinery, Inc., Lansing, Michigan, R. O. McKee, president, is reported planning erection of a 1500-barrel refinery at Lansing at reported cost of $100,000. Plans call for completion in September.

Refinery: Delbert Fortney, Mount Pleasant, Michigan, associated with the Strange & Fortney Oil Company, is reported having tentative plans for erection of a $350,000 refinery and cracking plant on a 12-acre site recently purchased in the village of Salzburg, near Bay City, Michigan.

Terminal: American Oil Company, marketing subsidiary of Pan American Petroleum & Transport Company, has completed plans for installation of a large terminal on the Monongahela River at Hays, Pa., near Pittsburgh. Cost reported at $1,000,000. Finished products will be barged from Pan American Refining Corporations' Texas City refinery via Gulf of Mexico and the Mississippi and Ohio rivers.

Solvent Plant: Gulf Refining Company, Port Arthur, Texas, will erect a 5000-barrel Furfural solvent process (The Texas Company, licensors). The company recently completed installation of an Acetone-Benzol solvent dewaxing process (The Texas Company licensee) with capacity of 1200 barrels per day at the Port Arthur plant. The company operates a Duo-Sol process plant at its Philadelphia refinery.

Terminal: Republic Oil Corporation, has converted the recently purchased refinery of Waverly Oil Works, at Coraopolis, Pa., into a large river terminal with 5,000,000 gallons capacity. The company is shipping gasoline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from its Texas City refinery to New Orleans by tanker and from that point by barge up the Mississippi and Ohio rivers to Pittsburgh. Republic Oil Corporation recently purchased the Pittsburgh stations of Shell Oil Company, giving it a total of 875 outlets in Pennsylvania, Virginia, West Virginia and Maryland.

Refinery: Inland Refineries, Pontiac, Michigan, is to build a refinery at Drayton Plains, Oakland County, Michigan. E. G. Guy, consulting engineer in charge. Estimated cost $80,000.

Combination Unit: Magnolia Petroleum Company, Beaumont, Texas, has signed contract with M. W. Kellogg Company, under Gasoline Products Company license, for construction of a 33,000-barrel capacity combination skimming, cracking and reforming unit.

Improvements: Magnolia Petroleum Company, Luling, Texas, is modernizing its skimming and cracking installation, including reconstruction of furnaces and other changes. Contract to Alcorn Combustion Company.

Gasoline Plant: Royalite Oil Company is building a new natural gasoline plant on the Sterling-Pacific lease, in the South Turner Valley, Alberta, Canada, field. To start operating in July.

Cracking Unit: The Model Refining Company, Reeds Switch, East Texas field, is erecting a cracking unit to increase gasoline recovery from East Texas crude. Skimming capacity is 1500 barrels daily.

Gasoline Plant: Means & McGehee, Inc., Houston, are reported planning construction of a natural gasoline plant to treat gas from C. B. Bunte's No. 1 Lackner, Eureka Heights district, near Houston. Project includes gas pipe line to service industrial concerns along the Houston Ship Channel.

Refinery: Denver Refining Company is to be formed by J. D. Cook, L. G. Smith and Ray Sims, Denver, Colorado, to operate a refinery now under construction at East 52nd St. and Colorado Boulevard, Denver. Capacity 500 barrels daily. To specialize in road and fuel oils.

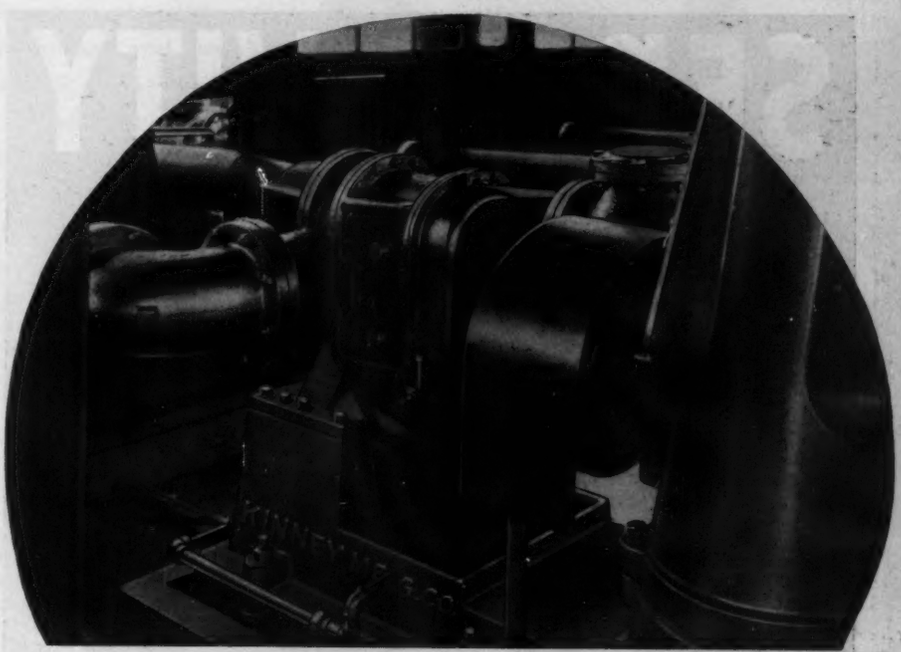
Gasoline Plant: Texas Carbon and Gasoline Corporation, W. T. Waggoner Building, Fort Worth, Texas, has been formed by Danciger Oil & Refineries, Inc., and David Rubin, to erect a 50,000,000 cubic feet natural gasoline plant and carbon black plant of sufficient capacity to handle residue. The two plants will be near Oil City, southwestern Hutchinson County, Texas Panhandle, and on the C. R. I. & G. Railroad. The company has leases on 16,000 acres of surrounding gas producing properties, including nine completed gas wells.

Refinery: Ray D. McGlothlin and Walter L. Jones, Abilene, Texas, are building a 500-barrel skimming plant on the Santa Fe railroad, at Goldsboro, Texas, to process high gravity crude produced on nearby properties of Centennial Oil & Gas Company in northwestern Coleman County. Part of the equipment was secured through dismantling the small topping plant at Echo, Texas, erected in July, 1931, by Echotex Refining Company, (later known as The Penn-Tex Producing & Refining Corporation).

Purchase: Eastern States Petroleum Company, which recently took over the Deepwater Refineries, Inc., plant on the Houston Ship Channel, Houston, for revamping and operation, has purchased a substantial interest in the Corpus Christi Refining Corporation plant, erected by G. L. Rowsey, et al., last year. This is a 1000-barrel cracking installation of modern type. Company also has purchased potential producing acreage in Southwest Texas recently.

Cracking: The Texas Company, Port Arthur, Texas, is including in its improvement and modernization program, plans for erection of a new combination skimming and cracking unit at reported cost of $850,000.

Improvements: Shell Petroleum Corporation, which is engaged in modernization of its refining facilities throughout the United States with notable construction work at Wood River, Illinois, and Arkansas City, Kansas, again is reported planning extensive additions and improvements at its Houston refinery with reports esti-



Kinney Pumps Save Fuel

by pumping lubricating oils with little or no heating!

16 motor-driven Kinney Pumps are installed in small individual pump houses just beyond the earth dykes on a certain tank farm. Large suction lines allow oil to be pumped at a maximum of 22″ vacuum at the pump. Smaller discharge lines and pumping pressures of 125 lbs. are used.

On many of these lines no heating is needed in the summer, on others very little. Temperatures run as low as 60° F. and on heaviest grades up to 130°F. (viscosities from approximately 100 SSU to 4000 SSU).

Total cost—pumps, houses, installation—was all paid for by the fuel saved in two years. **Other advantages: "bright stock" and "golden oils" retain their color better due to less heat; lower steam load made new boilers unnecessary. And, since they are Kinney Pumps, repair part costs have been pleasantly low.**

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mating expenditures from one to three million dollars, to be spent chiefly for large modern combination type cracking facilities.

Enlarge: Mid-Continent Petroleum Corporation, West Tulsa, Oklahoma, is reported planning erection of a new large Foster Wheeler distillation unit to be even larger than the recently completed unit at that plant. New equipment will replace presently operated shell distillation facilities.

Improvements: Continental Oil Company, Ponca City, Oklahoma, is planning to improve both its crude oil distillation and cracking facilities in the near future, according to current reports.

▼ BUSINESS NOTES ▼

THE Brown Instrument Company, Philadelphia, manufacturers of instruments and controls, and Minneapolis-Honeywell Regulator Company, Minneapolis, manufacturers of control systems and regulators, have opened a joint office at 303—the 101 Marietta Street Building, Atlanta, Georgia. A Minneapolis-Honeywell stock will be carried, and complete sales and installation service maintained at this office for the complete lines of both companies.

Wesley R. Moore, for a number of years district manager of Brown Instrument Company, is manager in charge, with Leon L. Kuempel, sales engineer, Charles A. Kitzinger, service engineer, and J. A. Crawley, office manager.

A. J. O'LEARY has been appointed assistant to general manager of sales at Lukens Steel Company, Coatesville, Pa. Prior to joining the Lukens organization in 1916, he was with the Pennsylvania Railroad and Alan Wood Steel Company. O'Leary spent five years in the mills and mill service departments at Lukens before he was transferred to the sales department, where he served since 1931 until his recent appointment as assistant to general manager of sales.

ROSS HEATER AND MANUFACTURING COMPANY, announces that its New York office recently has been moved and the present address is 40 West 40th St., New York.

WM. R. VAN NORTWICK, for many years identified with boiler and combustion work in the metropolitan territory, is now connected with the boiler sales division of Henry Vogt Machine Company, of Louisville, Kentucky, whose New York office is located at 80 Broad Street.

ROBERT F. KOCH, formerly with Foster Wheeler Corporation, now is representing the Henry Vogt Machine Company of Louisville, Kentucky, as boiler sales engineer in the Cleveland territory, with headquarters at 1005 Rockefeller Building, Cleveland, Ohio.

EFFECTIVE May 18, the Philadelphia district sales office of Republic Steel Corporation, and subsidiaries, Berger Manufacturing Company, and Union Drawn Steel Company was removed to the Broad Street Station Building, 1617 Pennsylvania Boulevard. J. B. DeWolf continues in charge of the office as district sales manager, assisted by the present staff.

GENERAL REFRACTORIES COMPANY, Philadelphia, Pa., announces appointment of Shadbolt & Boyd Company, Milwaukee, Wisconsin, as dealer agents in the Milwaukee area. Shadbolt & Boyd company will carry a complete stock of refractories.

GENERAL REFRACTORIES COMPANY, Philadelphia, announces appointment of Broadway Manufacturing Company, Knoxville, Tennessee, as dealer agents in the

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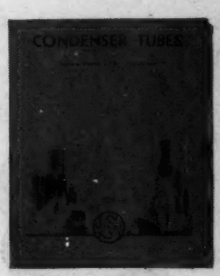
THE STORY BEHIND SCOVILL CONDENSER TUBES

NO SMALL part of the preference for Scovill Condenser Tubing in the oil industry rests on the interesting method by which Scovill produces Cup Drawn Admiralty—a tubing especially well suited to the conditions met in most refineries.

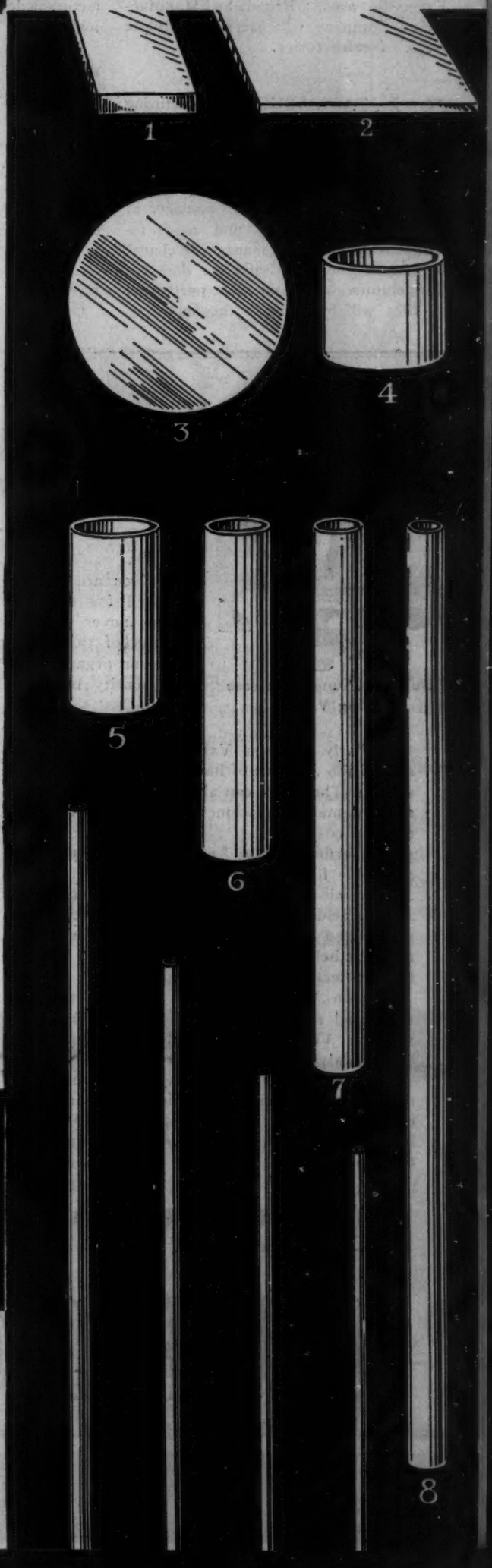
The alloy is first melted and cast into flat slabs (1) then rolled into heavy gauge sheet metal (2). Both top and bottom surfaces are milled and inspected with great care, for one side is to become the tube's inner surface. Blanking presses cut out discs (3), and draw them into heavy gauge cups (4). Only perfect metal can survive this cupping operation. Finally a series of presses and benches lengthens and thins the cups into tubes (5, etc.). Throughout this entire procedure controlled annealing relieves any metal strains produced by working and constant inspection eliminates any tubes with surface defects.

The finished tube is gauged for thickness, outside and inside diameters, concentricity again visually inspected, and tested under 1000 lbs. water and 80 lbs. air pressure. Samples are analyzed for grain size and checked for alloy, and others are subjected to tortuous bending, flaring and flattening tests.

Scovill engineers welcome discussion of your tubing problems. With years of experience and several proved alloys available, you will find them well qualified to help you. A free booklet — "Condenser Tubes" — will be mailed to interested persons. Write for it. Scovill Manufacturing Company, 13 Mill Street, Waterbury, Connecticut.



Standard Scovill Cup Drawn Admiralty Tubing stood up through flattening, bending, flaring and beading—to make this sample ash-tray!



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Detroit Chicago Cincinnati San Francisco Los Angeles

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Knoxville area. Broadway Manufacturing Company will carry a complete stock of refractories.

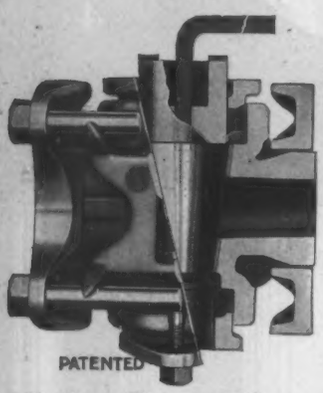
C. J. TAGLIABUE Manufacturing Company, Brooklyn, New York, announces appointment of E. D. Wacker as assistant general sales manager. Mr. Wacker has been with the company for 11 years, part of the time as manager of the Pittsburgh territory and, more recently, as division sales manager in charge of Snapon Controller sales for domestic refrigerators. A considerable portion of his time will be spent in the field contacting sales representatives as well as jobbers.

The company also announces that the sales of the Snapon Controller Division will be in charge of R. A. Skinner.

COMPAGNIA Tecnica Industrie Petroli S.A.I. of Milan, Italy, has consummated a license agreement with Chicago Bridge & Iron Works, Chicago, covering the sale, manufacture and erection of Wiggins Floating Roofs and Wiggins Breather Roofs for oil storage tanks in Italy.

Other firms licensed to manufacture Wiggins Roofs in foreign countries are Horton Steel Works, Ltd., Fort Erie, Ontario; The Motherwell Bridge & Engineering Company, Ltd., Motherwell, Scotland; The Whessoe Foundry & Engineering Company, Ltd., Darlington, England; Worms & Cie., LeTrait, France; and Asano Bussan Company, Ltd., Tokyo, Japan.

VULCAN Steel Tank corporation has about completed new offices in Tulsa to accommodate the recently formed Petroleum Division. It will engineer, manufacture and install gasoline plants and refinery equipment under the direction of



Duriron Plunger Release Plug Valve

VALVES . . . *that always work*

Valves are like men. Some are especially created for their jobs; always to be relied upon; never causing trouble.

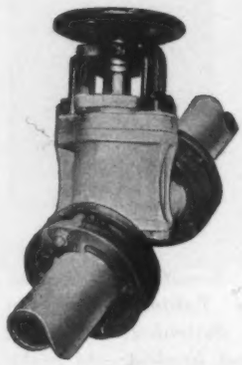
Men of this type constitute the backbone of your organization. They give you a sense of security in its future. You are proud of them.

Similarly Duriron Valves are built for a special job . . . that of handling acids and acid sludges. They, too, can always be relied upon; never demand replacement; hold down maintenance cost.

Furthermore, they are "utility" valves; adaptable for any acid service in the refinery . . . on unloading lines . . . at the concentrator . . . on acid transfer lines . . . at the treating plant. And even though there is grit in the material being handled, the hardness of Duriron protects it from scouring.

Duriron Valves are made in a variety of types and sizes, including Y Valves, Plunger Release Valves, Lubricated Plug Valves, Check Valves, etc.

The fact that Duriron Valves are in use in most of the principal refineries is convincing evidence that Duriron is best by test. When in need of corrosion-resisting valves, write us. Our specialized facilities are at your service.



Duriron Y Valves in sizes from 1" to 6"

Standard and special valves made in five different corrosion-resisting alloys for handling all kinds of acids.

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R. B. MILLARD

R. B. Millard, chief engineer, who for the past 16 years was designer for Southwestern Engineering Company equipment and represented that company in Tulsa as district manager and abroad as European representative. In addition to standard designs of exchanger and bubble tower equipment, the company will manufacture and market a new type of helical heater for heating crude, gas and air, a helical exchanger and other equipment and processes departing radically from conventional designs.

HERBERT J. WINN, president of Taylor Instrument Companies, Rochester, N. Y., sailed from New York, May 15, for London and a five-weeks business trip. A major part of his time while there will be spent at the plant of Short & Mason, Ltd., manufacturing distributors of the Rochester firm in Great Britain.

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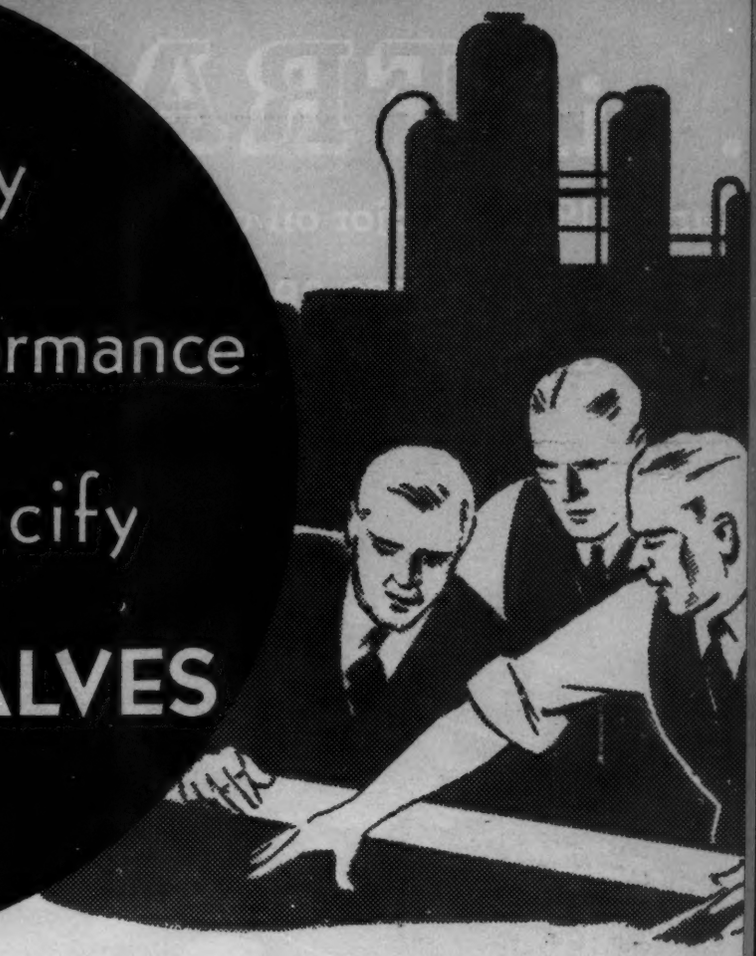

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Chapman Chrome Tungsten Steel Valves for corrosive service—pressures to 1500 lbs. and 1000°

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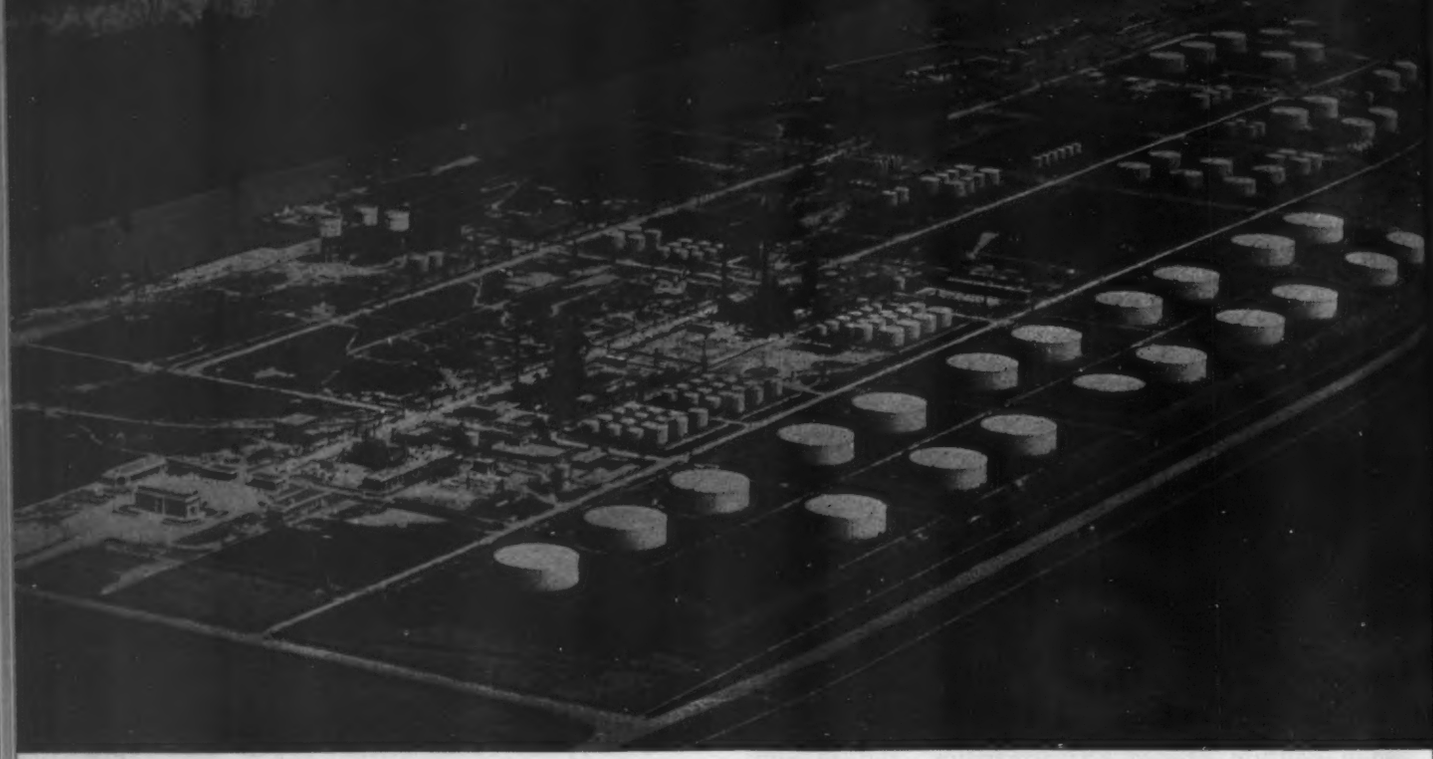
during 1935 a major oil company's second refinery will commence operation of a cracking unit under a Gasoline Products Company license



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SCIENCE AND TECHNOLOGY

Abstracts prepared in co-operation with the

REFINER AND NATURAL GASOLINE MANUFACTURER

by

THE LESLIE LABORATORIES

Traver Road, Ann Arbor, Mich.

under the supervision of

DR. E. H. LESLIE and DR. H. B. COATS

The abstracts here presented are selected from the current literature of science and technology to afford reference to fundamental information not easily available to all readers. Abstracts of articles appearing in readily obtainable trade journals are not included.

Photostat copies of original articles will be supplied at cost by the Leslie Laboratories. Complete or limited bibliographies covering special topics by title, by abstract, or in complete manuscript, will also be prepared and furnished at reasonable cost by the Laboratories.

Fundamental Physical Data

Critical Constants of Propane. J. A. BEATTIE, N. POFFENBERGER AND C. HADLOCK. *Jour. Chem. Physics,* **3** (1935), pp. 96-7.

The critical constants of C_3H_8 are: t_c=96.81 ∓0.01°, p_c=42.01∓0.02 normal atmosphere, v_c =0.195 l./mole (4.43 cc./g.), d_c=5.13 moles/l. (0.226 g./cc.). The uncertainty in the critical volume and density is 1%.

Heat Capacities and Dissociation Equilibria of Gases. B. LEWIS AND G. VON ELBE. *Jour. Am. Chem. Soc.* **57** (1935), pp. 612-4.

Accurate data covering heat capacities and dissociation equilibria derived from band spectroscopic data for gases have been gathered and arranged in two tables. The first table covers the energy content of hydrogen, oxygen, nitrogen, carbon monoxide, nitric oxide, water, carbon dioxide, ozone, bromine, and hydrobromic acid from 200° to 3500°. Table two gives the equilibrium constants for numerous equilibria involving these gases. Complete references to sources are included.

Vapor-Liquid Equilibrium Data for Commercially Important Systems of Organic Solvents. A. S. BRUNJES AND C. C. FURNAS. *Ind. Eng. Chem.* **27** (1935), pp. 396-400.

The authors comment on the increasing use of solvents for commercial purposes and the desirability of having more reliable distillation data for binary and more complex mixtures of these solvents in order to permit the effecting of their separation and purification. In the present article the liquid-vapor equilibrium curve for the binary system n-butanol n-butyl acetate, and n-butanol acetone are given. The composition for the azeotropic mixture of n-butanol n-butyl acetate was found to be 72.9 mol per cent alcohol and the boiling point 116.5°C. at 760 mm. The system n-butanol-acetone forms no constant boiling mixture.

Heats of Combustion and of Formation of the Normal Paraffin Hydrocarbons in the Gaseous State, and the Energies of their Atomic Linkages. F. D. ROSSINI. *Bur. Stand. Jour. Res.,* 13 (1934), pp. 21-35.

According to prevailing ideas, the heats of combustion of the paraffin hydrocarbons in the gaseous state should show constant differences between successive members of the series. Data for the first five normal paraffins show that, although the successive differences are not constant, they tend to approach a constant value with increasing number of carbon atoms. The generalization is made that in any organic molecule containing a normal alkyl group of more than five carbon atoms, the addition of a CH_2 group to the alkyl group to form the next higher normal alkyl group results in an increase in the heat of combustion in the gaseous state at 25°C. and 1 atmosphere pressure of 157.00∓0.08 kilogram calories of 15° per mole. Heats of formation can be most accurately computed from heats of combustion. However, it is necessary to know the heats of formation of liquid water and gaseous carbon dioxide. The heats of formation were calculated using the standard states of carbon as beta-graphite and diamond. The energy of dissociation of normal C_nH_{2n+2} (gaseous) into gaseous carbon and hydrogen atoms is a linear function of N if N is greater than 5. Deviations are given where N is less than 5.

Compressibility of, and an Equation of State for, Gaseous Ethane. J. A. BEATTIE, C. HADLOCK AND N. POFFENBERGER. *Jour. Chem. Physics,* **3** (1935), pp. 93-6.

The authors determine the compressibility of gaseous ethane over the pressure range 0.5 to 5.0 moles per liter, and temperature range 25° to 250°C. Ethane decomposes when in contact with steel above 250°C. An equation of state that has an average deviation of 0.21% was fitted to the data. The error is 10% when extrapolated to the critical pressure. The weight of a normal liter is given to 0.2%. The vapor pressure of liquid ethane at 0° is 23.57 normal atmospheres and at 25° 41.37 normal atmospheres.

Energies of Hydrocarbon Molecules. R. SERBER. *Jour. Chem. Physics,* **3** (1935), pp. 81-6.

The total energies of formation from the elements of propane, butane, butylene, 1, 2, 3, 4-tetrahydrobenzene, cyclohexane, acetylene, benzene, 1, 2-dihydrobenzene and naphthalene were calculated. The gross energies of the carbon-hydrogen, carbon-carbon, and double-bond carbon-carbon bonds were calculated from the observed energies of methane, ethane, and ethylene. Observed and calculated values agree well. However, the author regards the validity of any empirical bond additivity rule as merely fortuitous.

Critical Solution Temperatures of Some Hydrocarbons in Sulfur Dioxide. R. T. LESLIE. *Bur. Stand. Jour. Res.,* **13** (1934), pp. 589-597.

The separation of the components of the naphtha fraction of petroleum by the use of extracting agents boiling at about 0°C. was investigated. The solution temperatures in liquid sulfur dioxide of seventeen paraffin and naphthene hydrocarbons were determined. The results were correlated with the boiling-points of the hydrocarbons to study the possibility of separating nearly constant boiling-point mixtures. A few experiments were made using liquid ammonia and several aniline-points were determined for comparison. The relationship between boiling-point and critical solution temperature in sulfur dioxide is nearly linear for the normal and iso-paraffins from hexane to tetradecane. The line for the cycle hydrocarbons falls below that for the paraffins and is not regular. It was concluded that sulfur dioxide and ammonia show little promise as extracting agents. Aniline appears to be superior to the other two solvents.

Chemical Composition and Reactions

Separation of a Dimethylcyclohexane Fraction from an Oklahoma Petroleum. R. T. LESLIE. *Preprint, Am. Chem. Soc. Meeting,* New York City, April, 1935.

A monocyclic naphthene hydrocarbon was isolated from a fraction of an Oklahoma petroleum boiling at 119° to 121°C. By comparison with hydrogenated meta- and para-xylene it was judged that the naphthene from the petroleum was chiefly meta-dimethylcyclohexane. However, the isolated material was possibly an eutectic mixture of isomers with one in slight excess.

The Isolation of Ethylcyclohexane from an Oklahoma Petroleum. F. W. ROSE, JR., AND J. D. WHITE. *Preprint, Am. Chem. Soc. Meeting,* New York City, April, 1935.

A naphthene identified as ethlcyclohexane was isolated from a fraction of an Oklahoma petroleum that boiled 131-3°C. Comparison of the isolated material with synthesized ethylcyclohexane indicated a purity of about 95%. This hydrocarbon is present in the petroleum to an extent not exceeding 0.2%.

IV. Composition of Straight-Run Pennsylvania Gasoline. Fractionation of Straight-Run Gasoline. C. O. TONGBERG, D. QUIGGLE, AND M. R. FENSKE. *Preprint, Am. Chem. Soc. Meeting,* New York City, April, 1935.

Fractionation of straight-run gasolines from Pennsylvania and Michigan crude is described. The fractions showed wide variations in octane number, refractive index, and boiling range. Pennsylvania gasolines proved to be more complex in nature than Michigan gasoline. Narrow boiling range fractions were blended to produce a gasoline of higher octane rating than the original. The remaining fractions can be blended for use as Diesel fuel or for solvents.

The Separation of Petroleum Hydrocarbons with Silica Gel. A Simple Method for the Quantitative Removal of the Aromatic Components from the Naphtha Distillate of Petroleum by Adsorption on Silica Gel. B. J. MAIR AND J. D. WHITE. *Preprint, Am. Chem. Soc. Meeting,* New York City, April, 1935.

A number of binary mixtures of pure hydrocarbons, boiling from 80° to 175°C were separated by fractionation effected by filtration through columns of silica gel. The experiments showed that aromatic and olefin hydrocarbons can be completely removed from paraffin and naphthene hydrocarbons, that small but definite separations of naphthenes from paraffins occur, and that a slight separation of normal paraffin of different molecular weight

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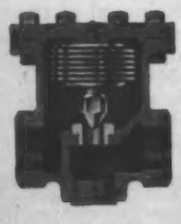

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also occurs, the paraffin of lower molecular weight being adsorbed in preference to that of higher molecular weight.

Sulfur Compounds of Technical Interest. The Isomeric Thiophthens. F. CHALLENGER AND J. B. HARRISON. *Jour. Inst. Pet. Tech.* **21** (1935), pp. 135-54.

The authors report an investigation of the thiophthens, the bicyclic sulfur compounds analogous to the monocyclic sulfur compound thiophen. The chemistry of these substances and the literature of the subject in general is reviewed in some detail. The experimental work in which the solid and liquid thiophthens were prepared from acetylene and boiling sulfur is described. Liquid thiophthen was prepared also from citric acid and phosphorus disulfide. The preparation of various derivatives is described.

Pyrolysis of Gaseous Paraffin Hydrocarbons. H. TROPSCH AND G. EGLOFF. *Preprint, Am. Chem. Soc. Meeting,* New York City, April, 1935.

The pyrolysis of gaseous paraffin hydrocarbons at temperatures of 1100 to 1400°C. and at 50 mm. pressure was studied. At 1100°C. propane and butane formed a maximum of 15 and 22 volumes of propylene per 100 volumes of hydrocarbon used, respectively. The maximum yields of acetylene from ethane and propane at 1400°C. were 53 and 76 volumes per 100 volumes of hydrocarbon used with a contact time of 6/1000 second. Methane required 10-20 times longer treatment at 1400°C. to form the maximum quantity of acetylene. The maximum obtainable yield of ethylene from ethane, propane, and normal butane is discussed.

Pyrolysis and Polymerization of Gaseous Paraffins and Olefins. F. W. SULLIVAN, JR., R. F. RUTHRUFF, AND W. E. KUENTZEL. *Preprint, Am. Chem. Soc. Meeting,* New York City, April, 1935.

The pyrolysis of ethane, propane, butane, and isobutane in KA2S coils is reviewed. Under optimum conditions a 75 to 100% by volume yield of olefins is secured. Paraffins higher than ethane decompose largely with formation of olefins and lower paraffins. The weight yield of olefins is less than the volume yield and averages about 60%. Results obtained in the polymerization of ethylene and propylene are reviewed. The polymerization runs were made at 500 to 3000 pounds pressure and under optimum conditions about 75% of the olefins convert to liquid.

Cracking and Polymerization of Low Molecular Weight Hydrocarbons. K. FROLICH AND P. J. WIEZEVICH. *Preprint, Am. Chem. Soc. Meeting,* New York City, April, 1935.

The thermal decomposition of methane, ethane, propane, normal butane, the corresponding olefins, and acetylene is discussed from the standpoint of maximum olefin and liquid fuel production. Simultaneous cracking and polymerization at atmospheric pressure is discussed and compared to cracking at atmospheric pressure for maximum unsaturate production followed by polymerization at high pressure and lower temperature. The removal of hydrogen increases the yield of liquid products almost four-fold. The introduction of air into heated olefins starts polymerization at much lower temperatures and pressures than if air is not present.

Catalytic Polymerization of Gaseous Olefins by Liquid Phosphoric Acid. V. N. IPATIEFF. *Preprint, Am. Chem. Soc. Meeting,* New York City, April, 1935.

Ethylene, propylene, and the isomeric butylenes were polymerized by phosphoric acid to liquid mono-olefins. The catalytic action of phosphoric acid depends upon its capacity to form esters that serve as intermediates in the formation of the polymers. The process has been effected in two steps as postulated. Various metallic salts and oxides promote the catalytic activity of the phosphoric acid. Individual olefins can be selectively polymerized in the presence of others. Naphthenes are formed under some conditions as a result of the cyclization of olefins. Paraffins and aromatics are formed as a result of hydrogenation-dehyrogenation reactions.

The Reaction between Oxygen and 2-Butene. H. J. LUCAS, A. N. PRATER, AND R. E. MORRIS. *Jour. Am. Chem. Soc.* **57** (1935), pp. 723-7.

The authors report the result of studies directed to determining the mechanism of oxida-

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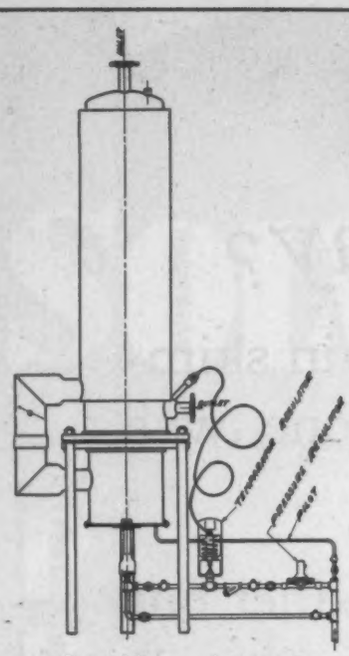

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tion of hydrocarbons. When a mixture of 2-butene and oxygen, with butene in excess, was passed through a hot tube at different temperatures between 375° and 490°C., the principal reaction products were found to be acetaldehyde and butadiene. Less important reaction products were glyoxal, an olefin oxide, acids, and some peroxide. At the higher temperatures octene was formed by a polymerization reaction. The results indicate that hydroxylation is not important in the oxidation of 2-butene, for no methyl ethyl ketone was formed and this substance would have been formed if hydroxylation were the first step. A probable reaction mechanism assumes the formation of 2-butene peroxide which decomposes into acetaldehyde. The other products are believed to have resulted from a succession of reactions that are already known.

Dependence of Methane-Oxygen Low-Pressure Explosion Limit on Nature of Reaction Vessel Surface. H. H. STORCH. *Jour. Chem. Soc.* **57** (1935), pp. 685-6.

Experiments were conducted to determine the low-pressure explosion limit of methane-oxygen mixtures using various surfaces of reaction vessel. The limiting pressures vary widely with the type of reaction surface employed.

The Effectiveness of Lead Tetraethyl in Increasing the Critical Compression Ratio of Some Individual Hydrocarbons. J. M. CAMPBELL, F. K. SIGNAIGO, W. C. LOVELL, AND T. A. BOYD. *Preprint, Am. Chem. Soc. Meeting,* New York City, April, 1935.

Quantitative measurements of the specific antiknock effect of lead tetraethyl in 62 individual hydrocarbons were made. It was found that there are variations as high as twenty-fold in the effectiveness of lead tetraethyl in suppressing knock in different hydrocarbons. General relationships between hydrocarbon structure and susceptibility to lead that appeared to be consistent within the scope of the work done, are described.

Products: Properties and Utilization

Light Effect on Color Stability of Gasoline. J. C. MORRELL, W. BENEDICT, AND G. EGLOFF. *Preprint, Am. Chem. Soc. Meeting,* New York City, April, 1935.

The effects of light on the color stability of Mid-Continent gasolines containing sulfur and normal propyldisulfide were studied using oxidizing, reducing, and inert atmospheres. In oxidizing atmosphere color, haze, peroxides, acids, and gum formed. Sulfur increased color, gum, and haze formation. The disulfides caused only color and haze formation. Exposure to non-oxidizing atmospheres caused no deterioration except in the case of those gasolines that contained sulfur, in which some color and gum formed. It was determined that particles causing haze contained sulfuric acid and organic matter.

Inhibitor Dyes in Cracked Gasoline. C. D. LOWRY, JR., G. EGLOFF, J. C. MORRELL, AND C. G. DRYER. *Ind. Eng. Chem.,* **27** (1935), pp. 413-15.

The extensive use of dyes in gasoline and the successful application of inhibitors to the stabilization of cracked motor fuel suggested a study of compounds possessing both coloring and inhibiting properties. In a study on the relationship of structure to inhibiting effectiveness, it was found that the presence of primary and secondary aromatic amino and aromatic hydroxyl groups usually conferred antioxidant power, and that the effect of these groups was increased by the presence of alkyl or tertiary amino groups, particularly when in the ortho or para position. The effects of chromophoric groups on inhibiting power had not previously been determined. Two indophenol dyes were prepared, indophenol and Phenol Blue. Both were found to be effective antioxidants. The corresponding leucoindophenols were even more powerful inhibitors.

Significance of Proknocks in Hydrocarbon Combustion. A. R. UBBELOHDE AND A. EGERTON. *Nature,* **135** (1935), p. 67.

Many substances have a mild proknock effect, but a special class has a pronounced proknock effect in concentrations as low as 10^{-5} and 10^{-6} mol. fraction. This special class includes organic compounds, the dissociation of

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which yields radicals of the types RO-, NO- and HO-. It appears that this disruption of an already oxegenated molecule may be common to many explosion processes that depend on chain branching. It is notable that the concentration required for proknock effect is smaller than 10^{-6}, since concentration of anti-knock substances of substantially the same order are required to prevent knocking.

Cold Test for Fuels. B. H. MOERBEEK AND A. C. VAN BEEST. *Jour. Inst. Pet. Tech.* **21** (1935), pp. 155-68.

Some fuel oils, particularly residual fuel oils, give a pour-point dependent upon the temperature of pre-treatment. To obviate this difficulty the A. S. T. M. maximum pour-point determination prescribes a temperature of pre-treatment. However, the A. S. T. M. pour-point as determined is not always the maximum, and secondly, in most cases, if not in all, a fuel oil will be freely flowing at a much lower temperature than the A. S. T. M. pour-point. On the other hand, the I. P. T. setting point is too low as determined, when compared with the results in actual practice. The dependency of pour-point on thermal history is occasioned by the presence of asphaltenes. If these substances are removed the fuel becomes temperature-insensible. The asphaltenes on cooling separate on the surface of the wax crystals, thereby preventing formation of a cohesive crystal structure. A new method of pour-point determination is proposed, which, although aiming at a maximum point, is better adapted to securing results in conformity with practical use. The oil is pre-cooled to eliminate the influence of asphaltenes on the wax, and pre-heated to such a temperature that the asphaltenes do not re-dissolve. In place of a pour-point, the pressure at which the fuel can be shifted is taken as a criterion.

The Aging of Mineral Lubricating Oils and the Products Therefrom. H. MULLER AND W. MULLER. *Montan. Rundschau,* **26,** No. 23 (1934), pp. 5-6.

Air was conducted through lubricating oil for 8 hours at 95°C. in the presence of different substances. Metals do not affect the saponification number, but metal oxides and metal salts increase it, as does also agitation of the oil. Water vapor, organic substances, such as resorcinol, pyrogallol and other hydroxyl compounds at a concentration of approximately 0.1%, acted as inhibitors of the oxidation. The aged oil was extracted with caustic soda and this in turn with petroleum ether. The liquid and solid products separated were studied.

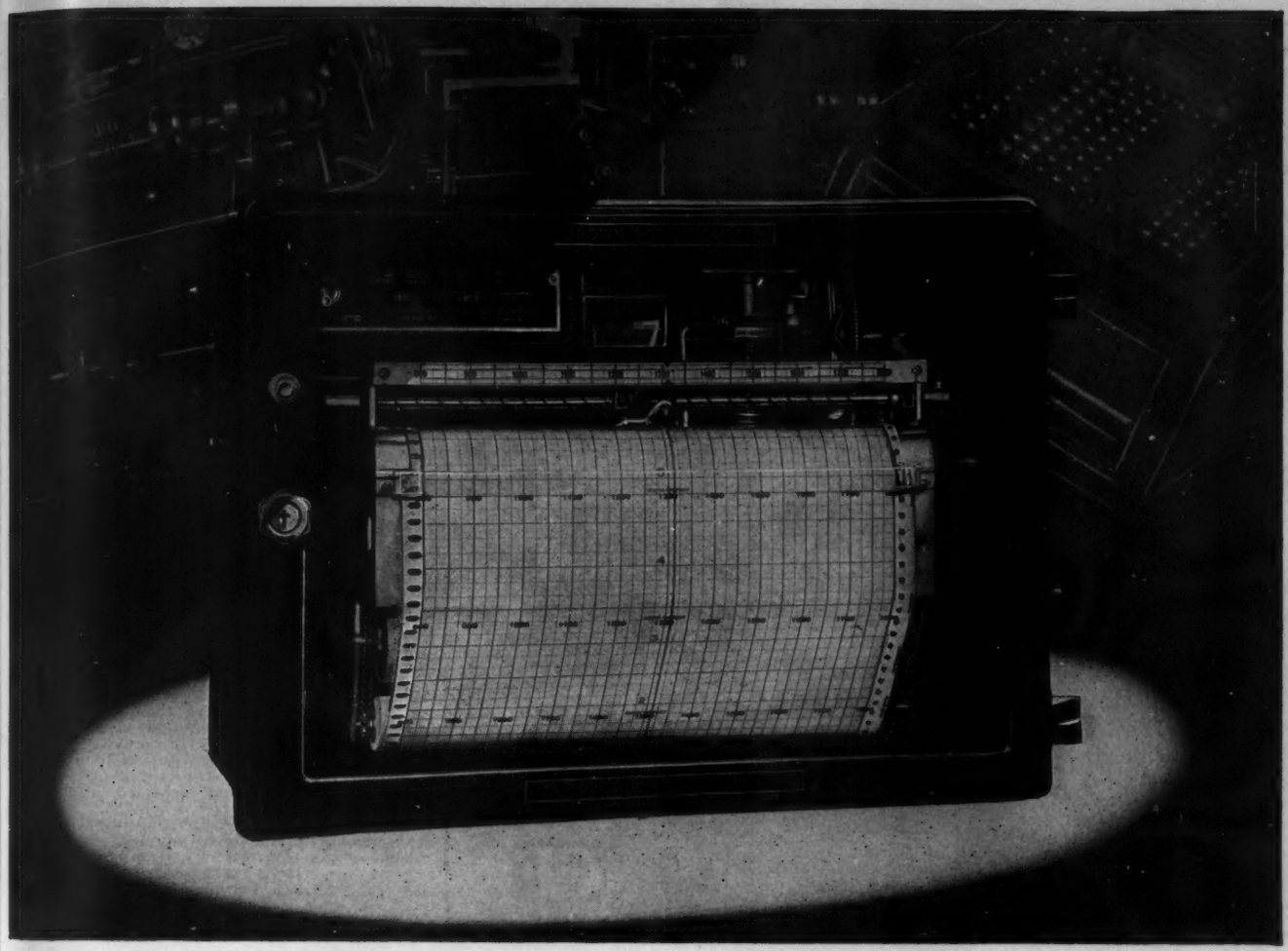
Manufacture: Processes And Plant

Aging of Mixtures of Transformer Oils. GOLDE. *De Ingenieur,* No. 45, (1934), E. 173.

Recent studies on the Continent contradict the views expressed by Forster and others that oil in transformers should be topped only with oil of similar origin and degree of refining. Weiss and Salomon (Conf. Int. des Grands Reseaux, 1931, Tl, p. 381) concludes from tests extending over a three-year period that the addition of fresh oil of different origin does not accelerate sludging. A commission has collected data from German power-stations over a period of several years (Mitt. der Studiengesel. fur Hochstspannungsanlagen e.v., Elektrizitatsbewirtschaft, 1934, p. 43) and their findings confirm those of Weiss and Salomon. In a few cases increase in sludging and acid formation occurred, but could be accounted for on the basis of the inferior nature of the original oil, the presence of material derived from the transformer, or excessive ageing of the original oil. Topping with fresh oil accelerates sludging only when the old oil is too much deteriorated. The following limits are suggested for aged oil: Saponification value greater than 1 — 1.4. No precipitation on standing 24 hours after mixing with 20 times its volume of normal benzine.

Boundary Lubricating Value of Mineral Oils of Different Origin. M. E. NOTTAGE. *Dept. Sci. Ind. Res., Lubr. Res. Tech.* Paper No. 2, 32 pp.

The effect of temperature on the boundary friction for steel and silver alloy surfaces of Burmese, Persian, Russian, asphaltic-base, and blended oils was studied. The oil was heated on the lubricated surfaces in air and in nitrogen. When the oil was dissolved in a solvent such as benzene or ether, placed on the surface and the solvent evaporated, the boundary friction curve was generally different from that for the oil itself. Two types of waxes were



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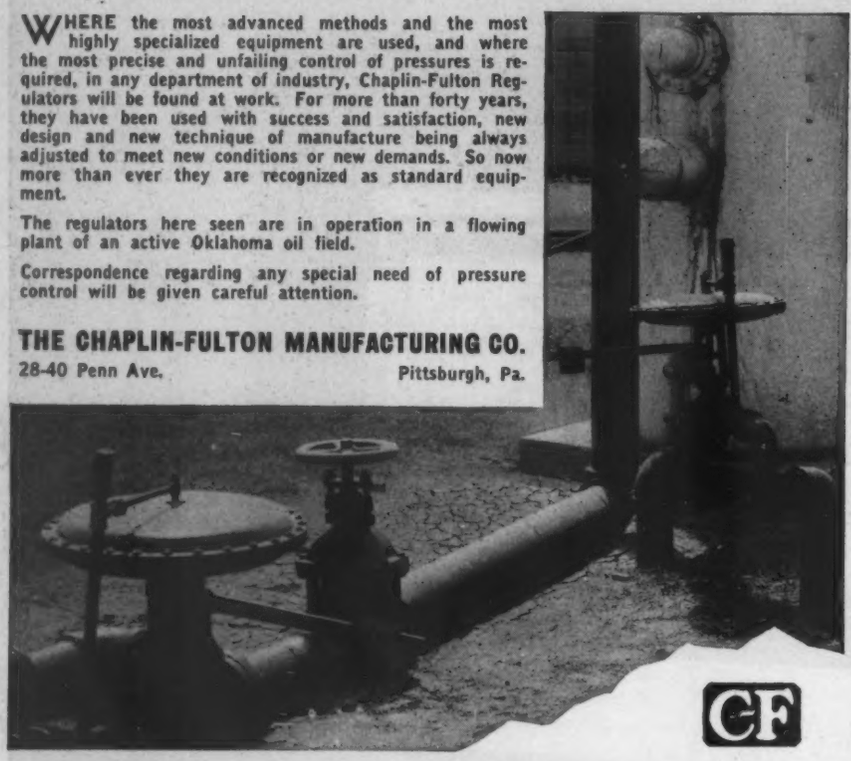

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found in the oil. The first type is readily separated from the oil as a white, oil-free, crystalline solid. The second type cannot be freed from oil even after prolonged fractional crystallization. Two types of boundary friction curves were found, the first given by distillate oils in which crystalline wax was found. In this case boundary friction remains constant or decreases as the temperature is raised from 18° to 60°, above which point it increases in air and to a smaller extent or not at all in nitrogen. The second is given by residual oils in which the second type of wax was found. In this case boundary friction increases as the temperatures is raised from 18° to 60° and then remains steady. The results are discussed and interpreted.

A Rapid Precision Viscometer. O. FITZSIMONS. *Preprint, Am. Chem. Soc. Meeting,* New York City, April, 1935.

A comparison, based on theoretical grounds, of the Saybolt viscometer with viscometers the efflux time of which is linear with viscosity, is made. The errors resulting from the use of Saybolt viscometer data in the calculation of viscosity index of light oils are discussed. The suspended level viscometer of Ubbelohde has been modified so as to allow the use of two capillary tubes of different bores and so as to permit mounting of the entire instrument in a vapor bath. The instrument is characterized by high inherent accuracy and can be used more rapidly than the Saybolt instrument.

Application of Graphical Method of Ponchon to Distillation and Extraction. E. W. THIELE. *Ind. Eng. Chem.* 27 (1935), pp. 392-96.

The author points out that most graphical methods for the computation of columns for the distillation of binary mixtures are based on the assumption that the overflow from plate to plate is substantially constant throughout the column. The method becomes inconvenient when this condition is not fulfilled. Ordinarily the fact that there is a temperature gradient throughout the column produces some variation in the overflow. This variation may become large if the temperature differences are large. In 1921 Ponchon presented a method which, while not so convenient as that assuming constant overflow, yet takes account of changes in overflow. This method is therefore applicable when the usual methods fail, as, for example, in distillation of materials in or near the critical region. Ponchon's method is explained and illustrated. A close analogy exists between distillation and counter-current liquid extraction. By a suitable modification, the method of Ponchon is applicable to extraction. The usual operation of this type is conducted in the equivalent of the critical region, with no rectifying section. The advantages of the use of a rectifying section and of a solvent in which neither component is completely miscible are pointed out.

Relative Efficiencies of Packed Fractionating Columns. P. DOCKSEY AND C. J. MAY. *Jour. Inst. Pet. Tech.* 21 (1935), pp. 176-99.

The authors derive equations from which the relative efficiencies of columns packed with materials of different shapes can be calculated. These equations are based on the assumption that the rate of interchange of material between vapor and liquid in a fractionating column depends upon the rate of diffusion through that part of the vapor in which the flow is streamlined. The equations apply both to the shape in which the flow of the total vapor is streamlined and to that in which it is turbulent. Terms are introduced that allow the effect of alternation of pressure and of vapor velocity, and the introduction of a diluent such as steam to be calculated. The derivation of the equations is given in detail. Tests were made using the system benzene-toluene in an 8 mm. diameter column 100 cm. long, operating at atmospheric pressure. For lower pressure work the system nitrobenzene-aniline was used in a column 2 inches in diameter. It was found that the experimental results correlated in terms of the chosen function.

Design of Fractionating Columns. II. Number of Plates for Gas and Gasoline Fractionators. G. G. BROWN, M. SOUDERS, AND W. H. HESLER. *Ind. Eng. Chem.* 27 (1935), pp. 383-92.

A method of computing the number of equilibrium plates required for the separation of complex mixtures is presented and compared in application to the results of theoretically rigorous calculations and also to test data from commercial equipment. The method is based

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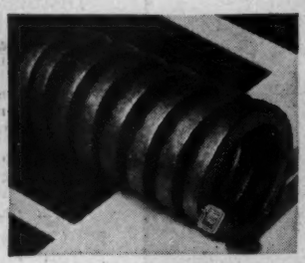

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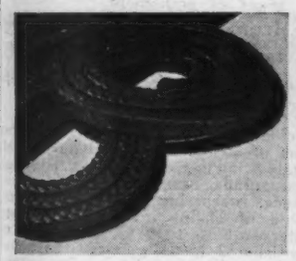

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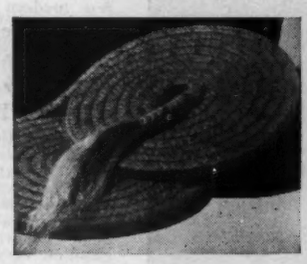

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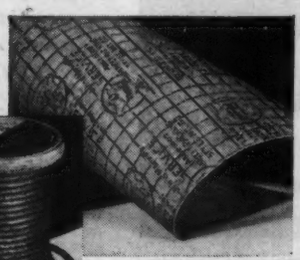

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on an adaptation of the absorption factor concept proposed by Kremser. This concept was previously applied by the authors to the design of gas absorbers and oil strippers. In the present procedure certain unsatisfactory assumptions previously used have been eliminated. The authors conclude that they present a simple and reliable method for the computation of the number of equilibrium plates required in commercial gasoline stabilizers and probably in similar equipment in which the equilibrium conditions between liquid and vapor may be assumed to follow the relationships of ideal solution.

A New Basic Principle in the Design of Fractionating, Absorbing, and Other Countercurrent Fluid Reacting Equipment. W. J. PODBIELNIAK. *Preprint, Am. Chem. Soc. Meeting,* New York City, April, 1935.

A new type of countercurrent fluid reacting apparatus was described. The operation is based on the use of controlled centrifugal force which permits the construction of compact apparatus and the use of high vapor and liquid velocities. Intimate contact between the phases is effected. The pressure drop through the apparatus may be small or negative.

Distillation. G. EGLOFF. *Chem. & Met. Eng.* **42** (1935), pp. 200-2.

The history of distillation is briefly reviewed from the time of Aristotle (350 B. C.) to the present. The article includes fifteen illustrations showing the stills of the alchemists, Samuel Kier's five-barrel refinery at Pittsburgh in 1855, one of the first refineries in Canada at Petrolia in 1870, the first refinery at Newhall, California in 1876, a typical cheese-box still as used in the Pennsylvania district, and several modern installations.

Heat Transfer. W. H. MCADAMS AND H. C. HOTTEL. *Chem. & Met. Eng.* 42 (1935), pp. 218-9.

The development of the subject of heat transfer, including combustion, convection, and radiation, is traced historically. The article is illustrated with several cuts showing heat transfer devices used in ancient times, as well as a few modern types of equipment.

Gasoline from Cracking Still Gases. V. N. IPATIEFF, B. B. CORSON, AND G. EGLOFF. *Preprint, Am. Chem. Soc. Meeting, New York City, April,* 1935.

A catalytic process has been developed for the conversion of olefins into liquid motor fuel. The solid catalyst is rugged and is not poisoned by hydrogen sulfide, carbon monoxide, nor other substances occurring in refinery gases. The conversion of olefins into liquid polymer is of the order of 80% to 95%. The yields of gasoline vary from 2 to 15 gallons. The liquid polymer consists of mono-olefins. Its octane number by the C. F. R. motor method is 80-85.

The Production of Gasoline by Polymerization of Olefins. C. R. WAGNER. *Preprint, Am. Chem. Soc. Meeting, New York City, April,* 1935.

Gases from low pressure vapor phase cracking operations containing 20 to 24% of ethylene, 13 to 18% of propylene, and 6 to 10% of unsaturates in the four-carbon group were polymerized through the action of heat and pressure but in the absence of catalysts. On a once-through basis 1.7 gallons of gasoline per thousand cubic feet were obtained at 950°F. and 800 pounds pressure. The yield was increased to 3.0 gallons by recirculating the gas derived from stabilizing the liquid products. In a commercial unit yields of 3.25 gallons were secured. Gas from stabilizing vapor pressure cracked distillates yielded 9.0 gallons per thousand. By operating at low pressure and 1200° to 1300°F. the liquid products were mostly aromatic.

The Hydrogenation of Bituminous Coal. M. PIER. *Ind. Chemist,* 11 (1935), pp. 139-48.

The author reviews the hydrogenation of coal and oil in Germany. Based on the results of experimental work, a full-size plant was built and operated at Leuna in 1926-1927 for the conversion of brown coal, brown coal tar, petroleum, and oil from bituminous coal tar. Simultaneously with the operation of this plant experiments were conducted on the hydrogenation of bituminous coal, the reserves and production of which are much greater in Germany than those of brown coal. A large-scale experimental plant having a capacity of one-tenth to one-twentieth of the proposed full-scale unit is now being operated at the Ludwigshafen-Oppau works.

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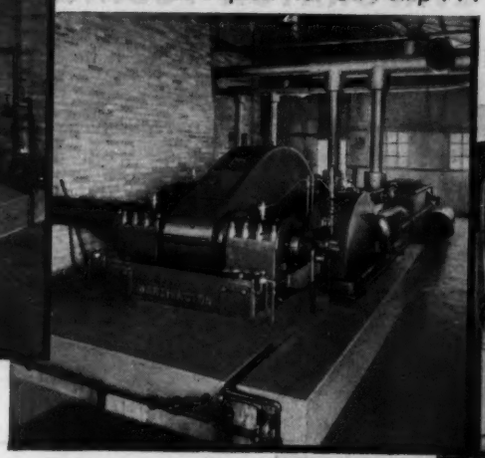

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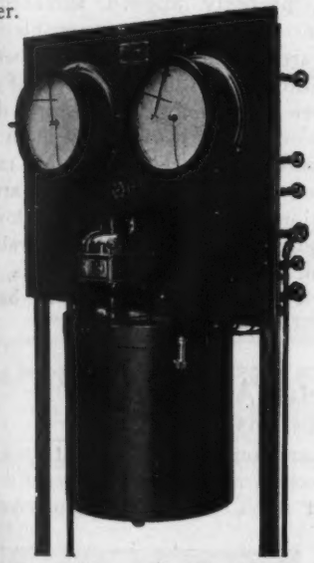
C. J. Tagliabue Manufacturing Company, Brooklyn, N. Y., has obtained the exclusive world-wide manufacturing and sales rights for a new Vapor Pressure Recorder. This outstanding device is a development of Industrial Engineers, Inc., of Los Angeles, California, under the Kallam patents and will be known as the TAG-Industrial Engineers Continuous Vapor Pressure Recorder.



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Now, instead of the long delayed results obtained from the Reid Laboratory test, it is possible with this recorder, to have a continuous record of vapor pressures instantly available. As vapor pressure is the most important single factor in the manufacture, blending and shipping of light petroleum products, the utility of this device will be appreciated. It now is offered after five years of experimental and development work and several years of plant service.

Vulcalock Valves

B. F. GOODRICH COMPANY.

B. F. Goodrich Company, Mechanical Division, Akron, Ohio, announces a rubber-lined valve of simple, rugged design and reasonable cost, suitable for handling corrosive and abrasive fluids under conditions of fairly high pressure, pulsating pressure, throttling or suction. Vulcalock valves may be lined with any of the standard Goodrich Acidseal compounds, hard or soft, depending upon conditions of service.

The action of the valve does not depend upon a flexible diaphragm. The resilient, rounded disc which snaps over a circular plate at lower end of stem provides an absolute seal when brought into contact with the molded rubber-covered seat rings. Both disc and seat ring are simple, inexpensive, easily replaceable parts. A steady, uniform flow and positive shut-off are obtained under severe operating conditions. Vulcalock valves may be used with perfect confidence for vacuum and throttling work, it is said.

Nearly straight line of flow renders the Vulcalock valve adaptable to fairly high pressure work and abrasive service.

The molded seat ring can be removed simply by taking off the body bolts. This ring is double seated and reversible for double service. By reversing the lower body section and replacing the bolts, the valve may be quickly changed from a straightway valve to an angle valve or vice versa.

The Acidseal lining of the valve is bonded to the metal parts with practically integral adhesion by the patented Goodrich Vulcalock process. Corrosive or abrasive materials handled come in contact only with rubber especially designed to resist their deteriorating action.

Oil Chiller

HENRY VOGT MACHINE COMPANY.

Henry Vogt Machine Company, Louisville, Kentucky, announces the development of the Vogt worm and gear driven, direct expansion oil chiller, protected by patent No. 1920570.

The Vogt direct expansion chiller was developed to meet the demand for extremely low temperatures with maximum efficiency. The liquid refrigerant is maintained at a predetermined level in the annular space of each pipe section regardless of the rapidity of evaporation. A constant contacted area of surface by the refrigerant is obtained, thereby maintaining maximum absorption efficiency. The horizontal position of the pipe sections and the unique design (patented) permits the passage of the gaseous refrigerant to the low side of the refrigerating machine without displacing any of the liquid refrigerant in the annular spaces of the pipe sections. The refrigerant gas is discharged from each pipe section so that the maximum expansion of the refrig-

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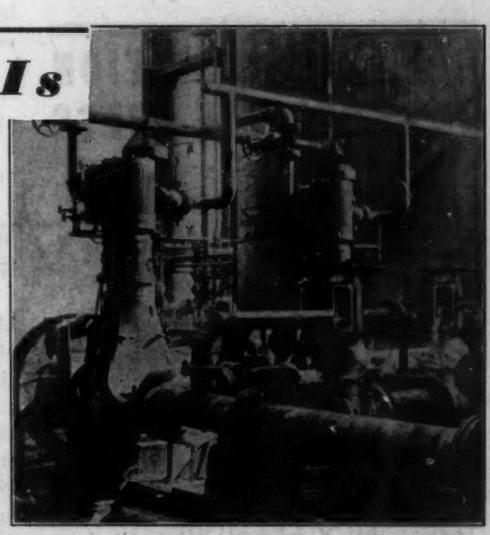

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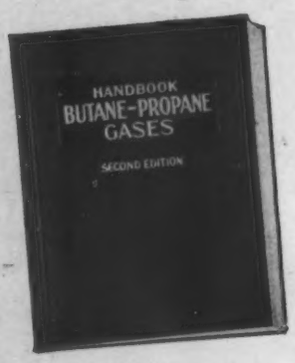

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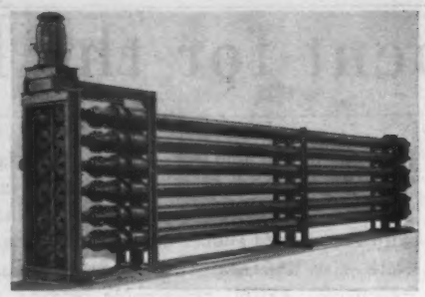

Vogt Oil Chiller

erant and consequent minimum temperatures are obtained in each pipe section. This design obviously overcomes the defect in chillers where the liquid refrigerant is expanded into the bottom section and fed serially upward through the unit.

Vogt direct expansion chillers, according to the makers, have the following advantages:

(a) The overall efficiency of the plant as a whole is greater because of the direct transfer of heat between the ammonia refrigerant and the oil to be cooled. Brine is eliminated as an intermediate cooling medium.

(b) Less surface is required for a given duty because the heat transfer rate is greater between the oil and the ammonia refrigerant than where brine is the cooling medium.

(c) Less power is required for pumping the oil because less surface is traversed.

(d) The elimination of an intermediate cooling medium (brine) also saves pumping power.

(e) No investment is required for a brine pump, motor and brine cooler.

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Midwest Pipe & Supply Company, 1420 South Second Street, St. Louis, Mo., announces a new line of stainless-clad welding ells which are formed by a ply plate having a thin inner or outer (as desired) surface of 18-8 stainless steel on carbon steel foundation. Longitudinal weld made with stainless rod on stainless face, high tensile rod on carbon steel face is also offered, as is stainless-clad pipe.

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THE YOUNGSTOWN SHEET & TUBE COMPANY.

The Youngstown Sheet & Tube Company announces a new alloy steel. This new product known as Yoloy is a nickel copper alloy steel, having an exceptional resistance to corrosion, high tensile strength combined with high ductility, workability and weldability. Yoloy steel is produced in sheets, strips, plates, bars, shapes, wire and seamless pipe.

Strainer

THE EDWARD VALVE & MFG. CO.

The Edward Valve & Manufacturing Company, East Chicago, Indiana, announces a line of forged steel strainers especially designed for high pressure, high temperature service, but available for low pressures and temperatures as well. Scale, dirt and grit increase the cost of maintenance and decrease reliability of piping equipment, such as traps, pressure regulators and the like which depend upon proper functioning of moving parts. Strainers serve to minimize such difficulties. The strainer bodies are said to be carefully selected forging quality steel, heat treated and accurately machined with full, properly aligned threaded pipe ends. The standard removable strainers are of perforated Monel metal. In addition to the cap for removal of the screen for cleaning purposes, a threaded pipe plug is provided through which accumulated foreign matter can be blown out. Screen dimensions are proportioned to give an effective flow area through the perforations equivalent to about seven times the pipe area, thereby lengthening the interval between cleaning periods.

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COEN COMPANY.

Coen Company, 917 Bryant Street, San Francisco, announces as a recent development the Coen Metal Atomixer with a special wire-feed mechanism that helps produce metallic coatings of uniform thickness at a saving in time. The atomizer will spray any metal that can be drawn into a wire.

Coen Metal Atomizer

Boiler Safety Device

MILLER FUEL ENGINEERING CO.

Miller Fuel Engineering Company, Houston, Texas, announces full production on the Miller low water fuel cutoff for prevention of boiler explosions or crown sheet failures due to low water conditions.

This cut-off was developed to provide a practical safety device for oil field type boilers, to stop the fuel supply

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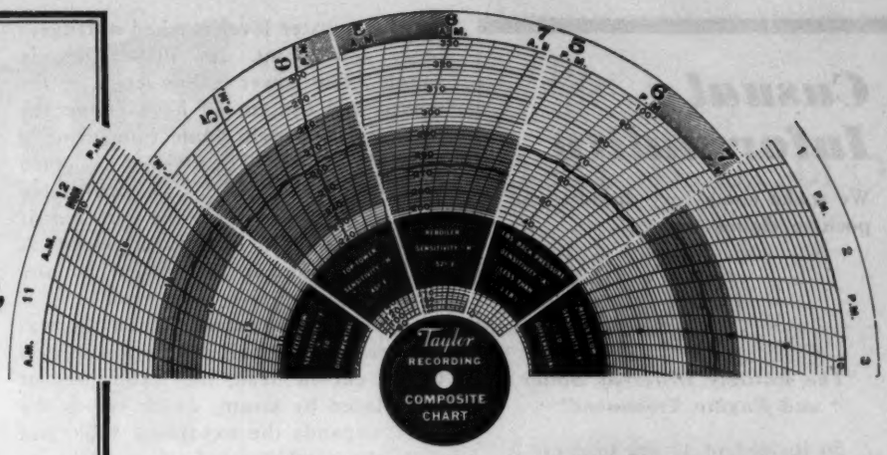

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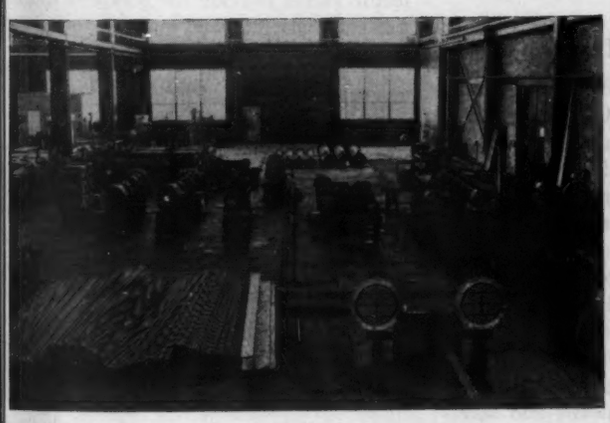

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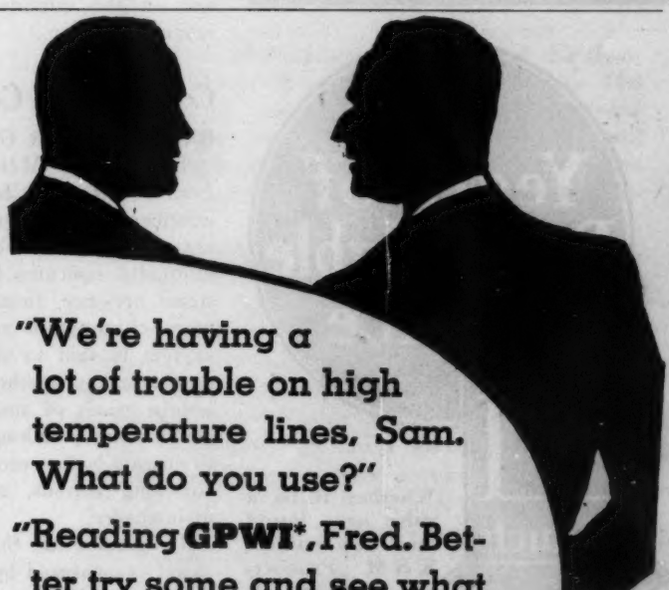

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when the water level reached a dangerously low point. Its installation is simple. The lower gauge cock is removed and the cut-off head connected to the gauge cock connection, using a ½" x 4" nipple. The tricock is then screwed into the head. The fuel valve is placed in the fuel line so that it closes when the lever arm drops. A chain is hooked in the trigger (in the head) and the valve lever arm.

Operation is positive. When the water level drops below the connection to the cut-off head, the water present is replaced by steam, which enters the head, expands the expansion tube, and pulls the catch away from the trigger. This drops the chain and closes the fuel valve. The trigger may not be reset until the water level is raised above the head. To reset, raise the water level and rehook the chain in the trigger. The valve is then opened and the boiler again fired.

The Miller cut-off is manufactured of brass and bronze materials to minimize adherence of scale. The lower tricock is connected to the cut-off so that any scale will be blown out when the fireman checks his cocks. Water in this cut-off is stationary, cool, and no evaporation takes place.

It operates on a pressure range of 0 to 500 pounds. The two working parts are on the outside, subject to ready inspection.

Combustion Control

BAILEY METER COMPANY.

The Bailey Meter Company, 1050 Ivanhoe Road, Cleveland, Ohio, announces development of a new air-operated combustion control which automatically operates boilers to maintain steam pressure, furnace draft and maximum combustion economy. This new system is said to simplify central station economy methods and place them within reach of small industrial boiler plants, thereby making it possible for them to operate boilers economically and safety for long periods, reducing outage and maintenance.

To accomplish this, the demand for steam is measured by variations in steam pressure and the rate of combustion is varied accordingly by the simultaneous control of fuel and air. This simultaneous control of fuel and air alone however, does not insure the highest combustion economy since the relationship between fan speed or damper position and air supply is not at all consistent and since stoker speed, feeder speed and oil or gas valve position does not hold a definite relation to the fuel supply, according to the makers. In order to overcome this difficulty, the new Bailey control system utilizes the steam flow-air flow relation of the Bailey boiler meter to readjust fuel or air supply so as to continuously maintain maximum combustion economy.

The control system is based upon the accurate measurement of all factors involved by recorders in which are incorporated frictionless free floating air pilot valves. These pilot valves are constructed so that they in no way decrease the accuracy or limit the operating ranges of the devices by which they are actuated.

Air is admitted at constant pressure to the space between two balls. Since the balls are of equal size, this results in a balanced valve. Being of slightly smaller diameter than the pilot valve sleeve, a small quantity of air escapes which tends to prevent actual contact between the balls and the sleeve and acts as an effective lubricant.

The pilot valve is used for operating control drives. Two outlets are connected to the control drive cylinder so that when the pilot valve is in a netural position the air pressure supplied to each side of the piston produces equal opposing forces and, therefore, the piston remains stationary. Should the pilot be moved slightly in either direction, increased air pressure would be admitted through one port to one side of the piston and air would be exhausted from the other side through one other port.

Flexibility of the control system is provided by selector valves on the master and individual boiler panels. These selector valves provide for complete or partial automatic control, manual control and boiler load adjustment.

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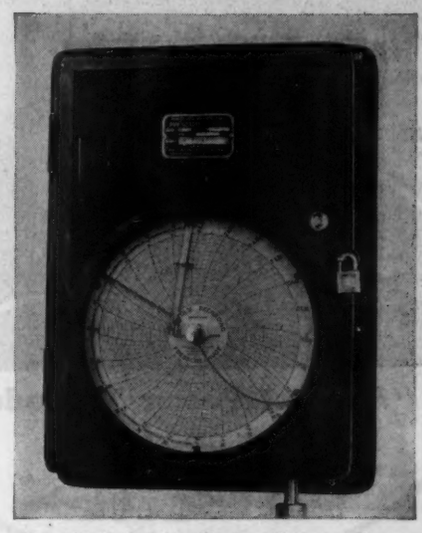

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"And a swell ratchet lever, snaps into forward or reverse. Or turn it to locked position, and I've got a solid die.

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"And RIDGID's a good looking tool, too—some satisfaction in keeping it cleaned up."

It is a distinctly better tool. Examine it at your Supply Store before you buy your next threader.

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have been used for steam boilers for 25 years and are now being used by leading oil companies for indicating oil levels in tanks, towers, stills, etc.

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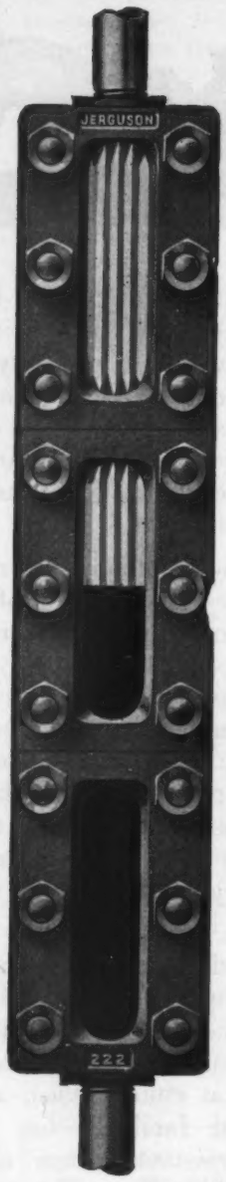

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CATALOGS . . . BULLETINS

Helpful Publications Which Manufacturers Will Be Glad to Send Free for the Asking

Glassware
Kimble Glass Company, Vineland, N. J., has issued Form 199, a 64-page book describing the company's complete line of blue-line calibrated laboratory glassware.

Power Generation
Combustion Engineering Company, 200 Madison Avenue, New York, has issued Catalog E-8, 16 pages describing its Type E—center retort, underfeed, stoker.

Technical Bulletin
Tube Turns, Inc., 745 South 5th Street, Louisville, Ky., has published a new technical bulletin on design of piping systems and the flow of liquids through pipes, including much information of value to engineers and others having to do with piping systems.

Steels
Republic Steel Corporation, Advertising Department, Massillon, Ohio, announces reprinted copies of the most recent revision of the list of standard S.A.E. alloy and carbon steel specifications are available upon request.

Condensate Pumps
Roots-Connersville Blower Corporation, Connersville, Indiana, is distributing a leaflet dealing with its newly developed self-priming automatic condensate pumps.

Spray Equipment
Binks Manufacturing Company, 3114 Carroll Avenue, Chicago, has published a new edition of Bulletin AD-114, 32-page catalog, giving prices and descriptions of new additions to the Binks line of spray equipment, spray guns, portable outfits, containers, extractors, hose, and exhaust units.

Instruments
H-B. Instrument Company, 2518 N. Board Street, Philadelphia, is distributing Bulletin 600, describing its line of dial and recording thermometers and humidity indicating instruments.

Mixing Equipment
Alsop Engineering Corporation, 39 West 60th Street, New York, is distributing a bulletin dealing with its lines of mixing equipment, filters, bottle filters, and glass coated tanks.

Colloidal Graphite
Acheson Colloids Corporation, Port Huron, Michigan, announces availabillty of a new technical bulletin No. 40R, pertaining to the application of colloidal graphite to industry, title "Foreign Bodies in Oil," subject material dealing with crank case analyses and deductions relative to sludging.

Flanges
Taylor Forge & Pipe Works, Chicago, has released a new 96-page catalog of text book type, containing much valuable data for those interested in the record of modern development in forged steel flanges.

Test Car
Refinery Supply Company, Tulsa, is distributing a new bulletin on the Gregory test car column for determining gasoline content of natural gas, gas and gasoline analysis in the field and operating efficiency for plants.

Centrifugal Pumps
Gardner-Denver Company, Quincy, Illinois, is distributing Bulletin CP11, dealing with its new line of centrifugal side suction pumps and including detail description, specifications and engineering data.

Chemicals
J. T. Baker Chemical Company, Phillipsburg, Pa., has issued its annual catalog of Baker's analyzed C. P. chemicals and acids and other laboratory and technical chemicals.

Potentiometer
The Brown Instrument Company, Philadelphia, is distributing a new catalog, No. 1101, dealing with the Brown petentiometer pyrometer for industrial service for indicating, recording and controlling temperatures.

Meters
The Foxboro Company, Foxboro, Mass, announces publication of a 48-page illustrated bulletin, No. 200, entitled "Meters for Steam, Liquids and Gas," covering the complete line of Foxboro meters for industrial usea. Construction details included as is much egnineering information on flow measurement.

Water Treating
Rathbun Company, Inc., El Paso, Texas, has published Bulletin E-30, dealing with the chemically and mechanically controlled Rathbun system of treating cooling waters for prevention of scale, rust and corrosion in Diesel and gas engines, condensers, compressors, air washers, humidifiers, refrigerating plants and all circulating waters.

Control
C. J. Tagliabue Manufacturing Company, Park and Nostrand Avenues, Brooklyn, N. Y., is distributing an eight page folder describing the Tag-Industrial Engineers Continuous Vapor Pressure Recorder. Full engineering information given and well illustrated.

Electrodes
Metal & Thermit Corporation, 120 Broadway, New York, is distributing a new bulletin devoted to Murex all-mineral coated welding electrodes. Considerable technical data, including principles of design and operation as well as physical properties and chemical analyses of deposited metals are given. The 16-page book is fully illustrated.

Wire Cloth
Newark Wire Cloth Company, 351-365 Verona Avenue, Newark, New Jersey, is distributing an illustrated four-page folder illustrating and giving data on wire cloth products, giving typical weaves and meshes, shows such products as testing sieves, end shake testing sieve shaker, metallic filter cloth, gasketed metallic filter cloth, and the like. Condensed price list included.

Electrical Equipment
Allis-Chalmers Manufacturing Company, Milwaukee, Wis., is distributing the following bulletins: No. 2100, entitled "Wound Rotor Induction Motors, No. 2183," Type E direct current motors and generators, and No. 2199, entitled "A useful pumping unit for every industry."

Pumps
Gardner Denver Company, Quincy, Illinois, is distributing a new bulletin describing single stage, its double suction, split case, types D, E, F, and G, centrifugal pumps.

Equipment
Worthington Pump and Machinery Corporation, Harrison, N. J., has published the following bulletins recently: W-318-B6A- Worthington two stage volute, type U, centrifugal pumps; L-620-B 8, Worthington two stage, type VA-2, vertical angle air compressors; L-621-B6- Worthington single stage, type VS, vertical single air compressors; W- 102-B1- Worthington turret type horizontal duplex piston pumps for handling liquids at pressures up to 200 lb. per sq. in.; and W-321-B2A- Worthington, Group D, single stage Monobloc centrifugal pumps.

Cable Accessories
General Electric Company, Schenectady, N. Y., as a companion book to GEA-1731, "How to Make Cable Joints" issued last year, now has available a new publication GEA 1839 "Cable Accessories", listing and describing all the materials necessary for making cable joints. It is an 80-page book, complete with illustrations, information and includes prices.

Feeder
Hardinge Company, Inc., York, Pa., has issued Bulletin 33 C, describing the Hardinge constant weight "B" feeder with variable speed drive and the non-flooding constant weight feeder for materials that "aerate" and "flood."

Equipment
Ross Heater & Manufacturing Company, Buffalo, N. Y., announces availability of five new catalogs as follows, Form 1037, Sterling Oil Section Catalog; Form 1039, Ross Expansion Joint Catalog; Form 1040, Arco Metal Pipe Catalog; Form 1041, Ross Storage Tank Heater and Form 1043, Ross Decalorator (Steam Jet Refrigeration) Catalog.

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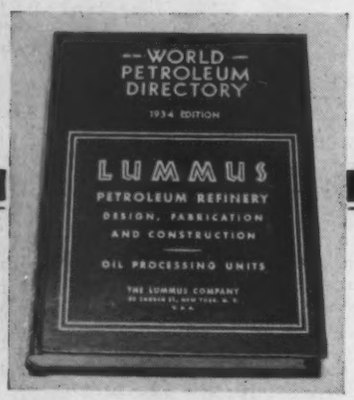

World Petroleum Directory 1934 EDITION

This book covers the oil companies of the entire world, listing producers, refiners, marketers, and jobbers, pipe line and transport operators, natural gasoline manufacturers, giving complete information regarding directors, officers, personnel, subsidiaries, history, capital structure, dividends, detailed information concerning properties and financial reports for 1933 as well as quarterly reports for 1934. It also contains an up to date list of oil associations, asphalt manufacturers and producers of liquefied petroleum gases. A special section is devoted to United States marketers and jobbers of petroleum products, arranged by states. Oil companies operating outside of the United States have been segregated by continent and country in order that the data may be obtained easily. The edition also contains a list of refiners of the world which has been arranged by states and countries. Chart of Soviet petroleum industry shows the producing, refining, marketing and pipe line properties. This section also contains a list of the directors of the Soviet trusts.

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